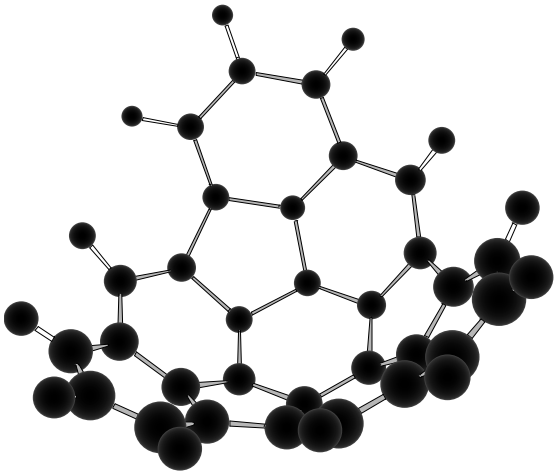
Catalytic Cleavage of Carbon-Carbon Sigma Bonds Using Transition Metals

Author: James Michael Dombrowski



Catalytic Cleavage of Carbon-Carbon Sigma Bonds Using Transition Metals

BY JAMES MICHAEL DOMBROWSKI

Boston College Department of Chemistry
Professor Lawrence T. Scott, Research Advisor

A *Scholar of the College* project in organic chemistry

May 2005

Abstract

The focus of this project was to probe the ability of various transition metal complexes to cleave carbon-carbon bonds in a $C_{30}H_{12}$ hemifullerene. The hemifullerene was synthesized in our lab from commercial 1-tetralone and bromonaphthalene in six steps. Palladium and nickel complexes were used to open the five membered rings along the periphery of the $C_{30}H_{12}$ bowl. Diphosphine complexes of nickel were capable of opening either all three five membered rings or one of the periphery five membered rings and the central six membered ring.

I never let my schooling interfere with my education.
-Mark Twain

Acknowledgements

I would like to take this opportunity to thank those people who have helped me over the past four years.

To my parents, you taught me to work hard and stand by my beliefs. Without your support and love, I would not have made it this far. I appreciate all that you have given me, and I hope I have made you proud.

I would like to thank my brothers, Mike and John who, always remind me what is truly important in the world.

I want to thank my friends who have been with me through the ups and downs of college life. I wish you all the best as we set off on our separate paths.

To the members of the Scott Lab – Pat, James, Ronald, Mihai, Tom, Vikki, Xiang, Ed, Aaron, Tony, Jon, Ricky, and Chris, it has been a true pleasure working with you over the past three years. Thank you for your patience with my questions and for making the lab a great place to work.

To Lingqing, who took me under her wing and taught me how to be a chemist. I would not have gotten this far without your patience and knowledge. I wish you the best as you move beyond Boston College.

And to Dr. Scott, who is a rare combination of intelligence, wisdom, kindness, and class. It has been a privilege to learn from you and a pleasure to work for you.

Regards,

James Michael Dombrowski

April 2005

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Chapter II: Synthesis of $C_{30}H_{12}$ Hemifullerene

List of Symbols and Abbreviations

^{o}C	degrees centigrade
d	doublet
δ	chemical shift in parts per million
depe	1,2-bis(diethylphosphino)ethane
dippe	1,2-bis(di-*i*-propylphosphino)ethane
dppm	1,2-bis(diphenylphosphino)methane
dppp	1,2-bis(diphenylphosphino) propane
DCE	1,2-dichloroethane
FVP	flash vacuum pyrolysis
g	gram
HOMO	highest occupied molecular orbital
Hz	Hertz
J	coupling constant
LUMO	lowest unoccupied molecular orbital
m	multiplet
M	moles per liter
MHz	megahertz
mL	milliliter
mmol	millimoles
mp	melting point
MALDI	matrix assisted laser desorption ionization spectrum
MS	mass spectrum (low resolution)
NMR	nuclear magnetic resonance
PAH	polycyclic aromatic hydrocarbon
ppm	parts per million
p-TsOH	para-toluenesulfonic acid
s	singlet
t	triplet
THF	tetrahydrofuran
TLC	thin layer chromatography

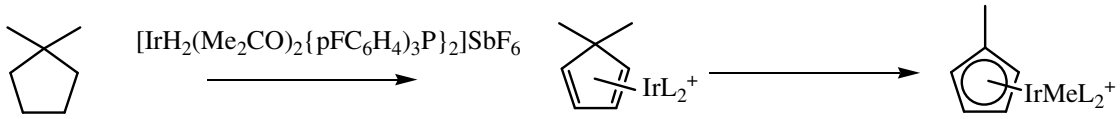
Chapter I: Introduction

1.1 Routes to Cleavage

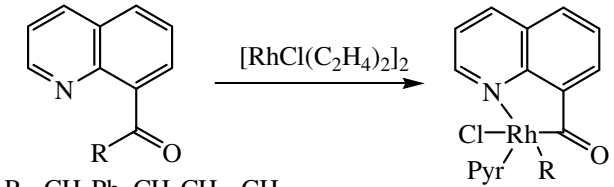
The discipline of organic chemistry is based upon the bonds formed between carbon and other atoms. Of these bonds the most important and the most versatile are between carbon and itself. The main focus of this discipline is to form bonds between carbons, but also important is the ability to activate and break existing carbon bonds. Techniques that effectively activated carbon-carbon bonds under mild conditions have applications in both synthesis and the petroleum industry. An attractive route to the activation of carbon-carbon bonds is through the use of transition metal complexes.

As the carbon-carbon bonds of hydrocarbons are very stable, some driving force is generally needed to selectively cleave these bonds instead of the more accessible carbon-hydrogen bonds. Traditionally, four routes have been used to cleave carbon-carbon sigma bonds with transition metal complexes (Fig 1): the drive to aromaticity in pre-aromatic compounds,[1a-k] activating functionality,[2a-e] forced proximity between transition metals and carbon bonds,[3a-k] and relief of strain.[4a-r] Of these four routes, the most well known is the use of strain first demonstrated by the opening of cyclopropane with platinum by Tipper in 1955.[4a]

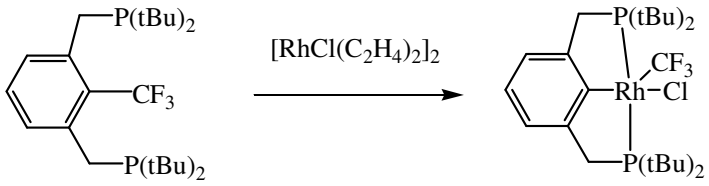
Drive to Aromaticity



Activating Functionality



Forced Proximity of Metal



Relief of Strain

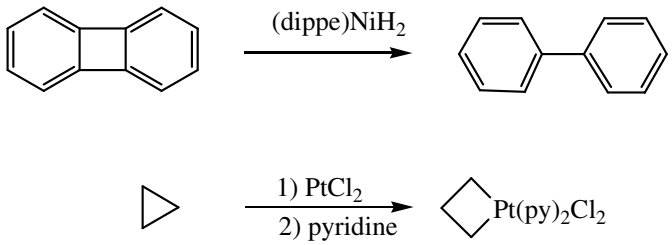


Figure 1: Four traditional routes to cleavage of carbon-carbon sigma bonds: drive to aromaticity,[1a] activating functionality,[2a] forced proximity of the metal,[3k], relief of strain in three[4a] and four[4q] membered rings.

1.2 Objective and Initial Experiments

Most examples of the use of strain as a driving force for the cleavage of carbon-carbon bonds using transition metals involve either three or four membered rings. Of those transition metal complexes that activate carbon-carbon bonds, only very few are known to do so catalytically.[5a-h, 4q, 3b] To our knowledge catalytic hydrogenolysis of carbon-carbon bonds in homogenous solution has been achieved on three occasions.[5e,h,i]

Our goal is to use various transition metal complexes to open the strained five membered rings in the $C_{30}H_{12}$ hemifullerene, **6**. This fullerene fragment has been synthesized in our lab and as the curvature in the molecule creates a great deal of strain, we feel that it is an ideal candidate to probe the limits of carbon-carbon sigma bond cleavage. From the starting material (**6**) we expect to get four products (Fig. 2), with each successive cleavage releasing progressively less strain.

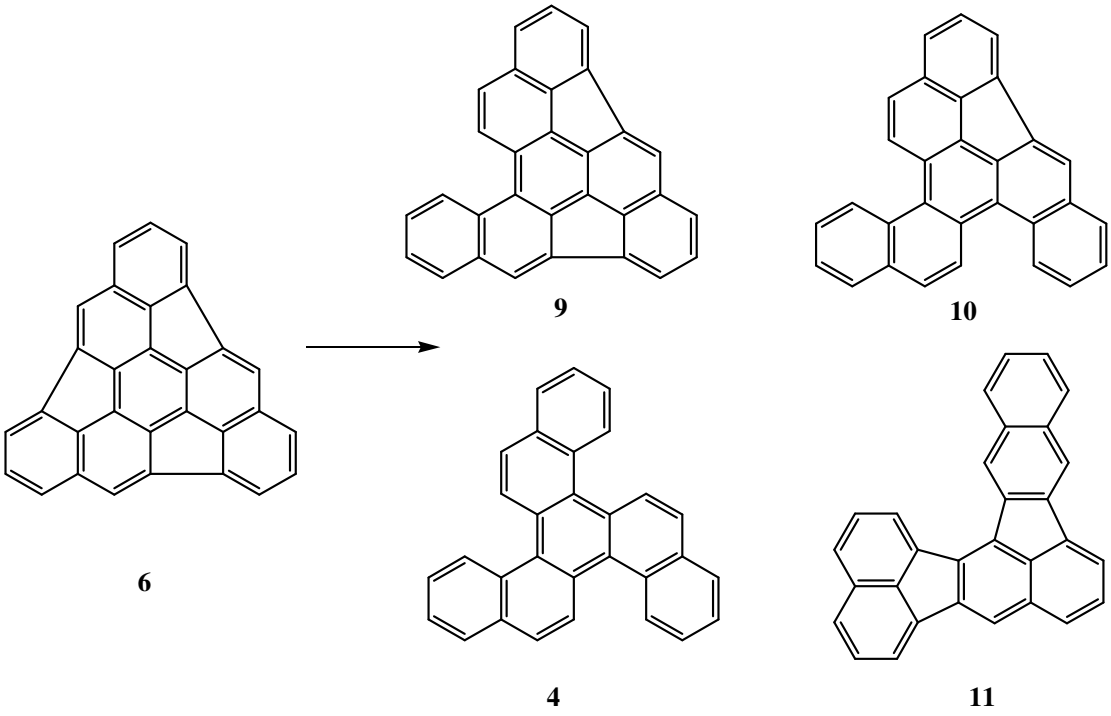


Figure 2: Expected cleavage products of hemifullerene **6**

If it were possible to open all three of the five membered rings in compound **6** to form compound **4**, it would represent considerable progress in probing the abilities of transition metal complexes to activate carbon-carbon bonds.

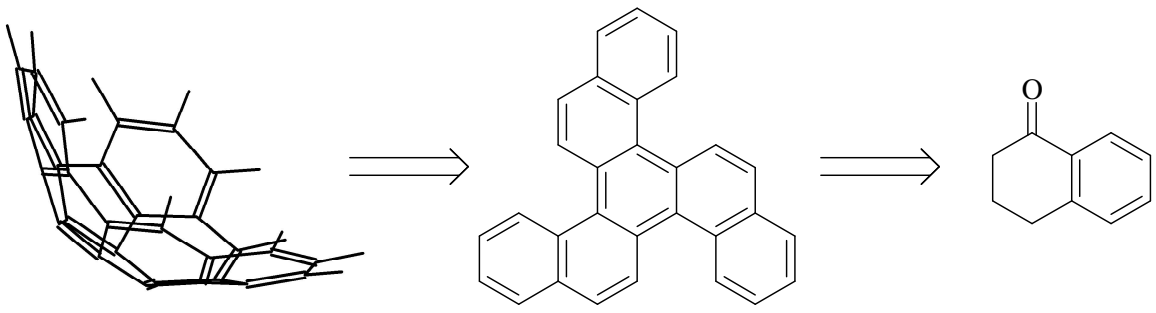
Chapter II: Synthesis of $C_{30}H_{12}$ Hemifullerene

2.1 Objective

For some years now, the Scott Group has focused on the synthesis of curved polycyclic aromatic hydrocarbons from relatively planar starting materials.[6] Producing curvature in large conjugated systems produces a great deal of strain in the molecules. FVP has proven to be an invaluable tool to overcome the energy barrier required to make curved molecules from flat starting materials. The synthesis of hemifullerene **6** has been completed in six steps.[7] This ring strain would then provide the driving force to break the relative weak bonds in the five membered rings.

2.2 Retrosynthetic Analysis

Retrosynthetic disconnection of the target molecule **6** provides benzonaphthochrysene **5,** as a pyrolysis precursor (Fig. 1). Benzonaphthochrysene can be further disconnected to yield 1-tetralone as a starting material.



6 **5**

Figure 1. Retrosynthesis of $C_{30}H_{12}$ Hemifullerene (**6**)

For successful formation of the target molecule **6**, six carbon-hydrogen bonds must be broken followed by the formation of three carbon-carbon bonds. The 1-tetralone did not trimerize as expected to give the hexahydrobenzonaphthochrysene. Instead, the aldol condensation stopped at the dimer. Therefore, 2-naphthyl lithium was used to add the additional ten carbon atoms. As the pyrolysis of the hydrocarbon precursor was expected to give very low yields of product, it was brominated at the 6,12, and 18 position. The low bond energy between carbon and bromine allows for homolytic thermolysis at high temperatures (Fig. 2). A 1,2-hydrogen shift then takes place.[8] This is followed by formation of the carbon-carbon bond and loss of a hydrogen atom to rearomatize.

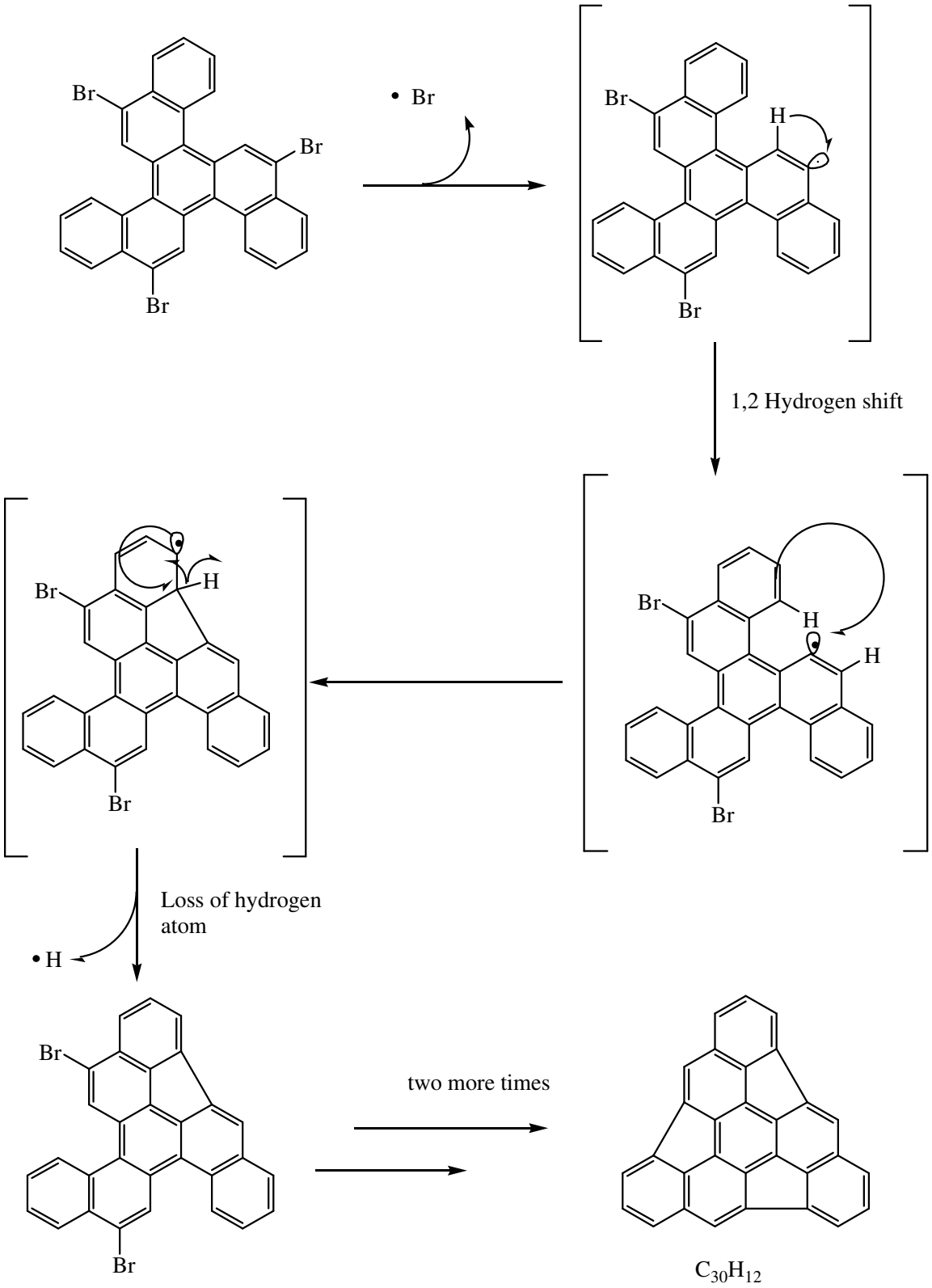


Figure 2. Formation of $C_{30}H_{12}$ (**6**) through loss of bromine and 1,2-hydrogen shift

2.3 Flash Vacuum Pyrolysis

Flash vacuum pyrolysis has proven to be a useful technique to form fullerene fragments from planar PAHs. In the pyrolysis of tribromobenzonaphthochrysene, a sample is placed in a quartz boat. The boat is then placed in quartz tube lying within two ovens. The quartz tube is then connected to a nitrogen inlet. The nitrogen flow is used to aid the sublimed compound through the second oven and into the cold trap. On the other end, the tube is connected to a cold trap, a manifold, a second cold trap, and then to a vacuum. A mercury monometer is connected to the manifold between the two cold traps (Fig.3). The first oven contains the sample and is heated to 150 ^{o}C to 220 ^{o}C to sublime the sample. The second oven, where the reaction takes place, is heated to 1050 ^{o}C. The product is then collected in the first cold trap which is cooled by liquid nitrogen in a Dewar flask.

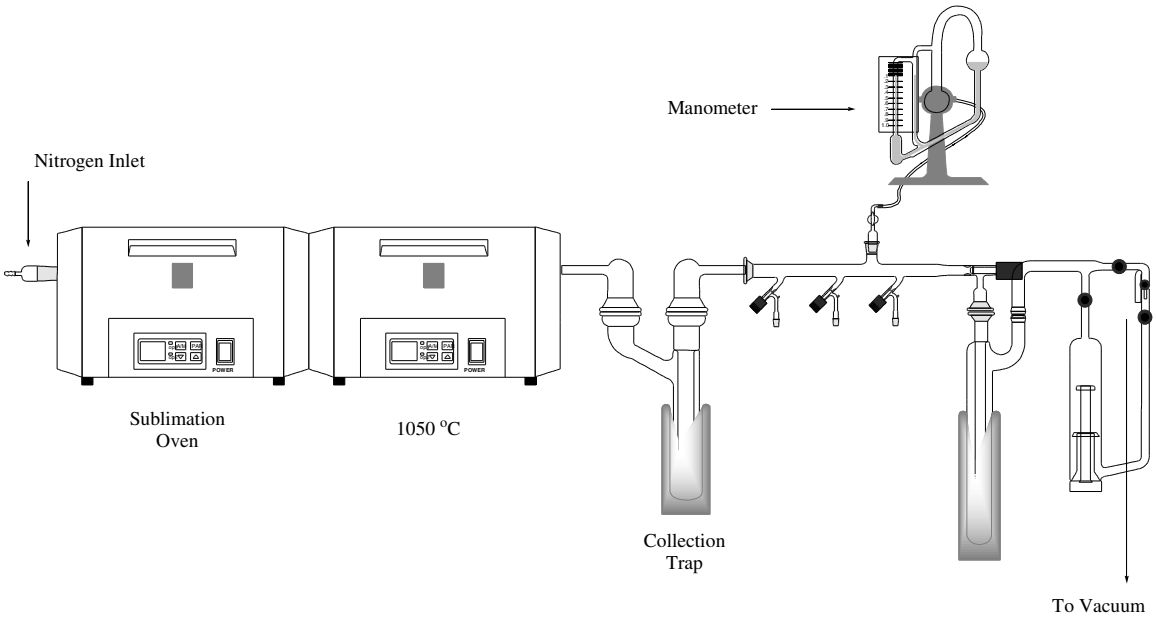


Figure 3. Flash Vacuum Pyrolysis Apparatus

2.4 Results and Discussion

The $C_{30}H_{12}$ is produced in six steps from commercially available 1-tetralone and 2-naphthyl lithium (Fig. 4). This chiral molecule represents 50% of buckminsterfullerene.

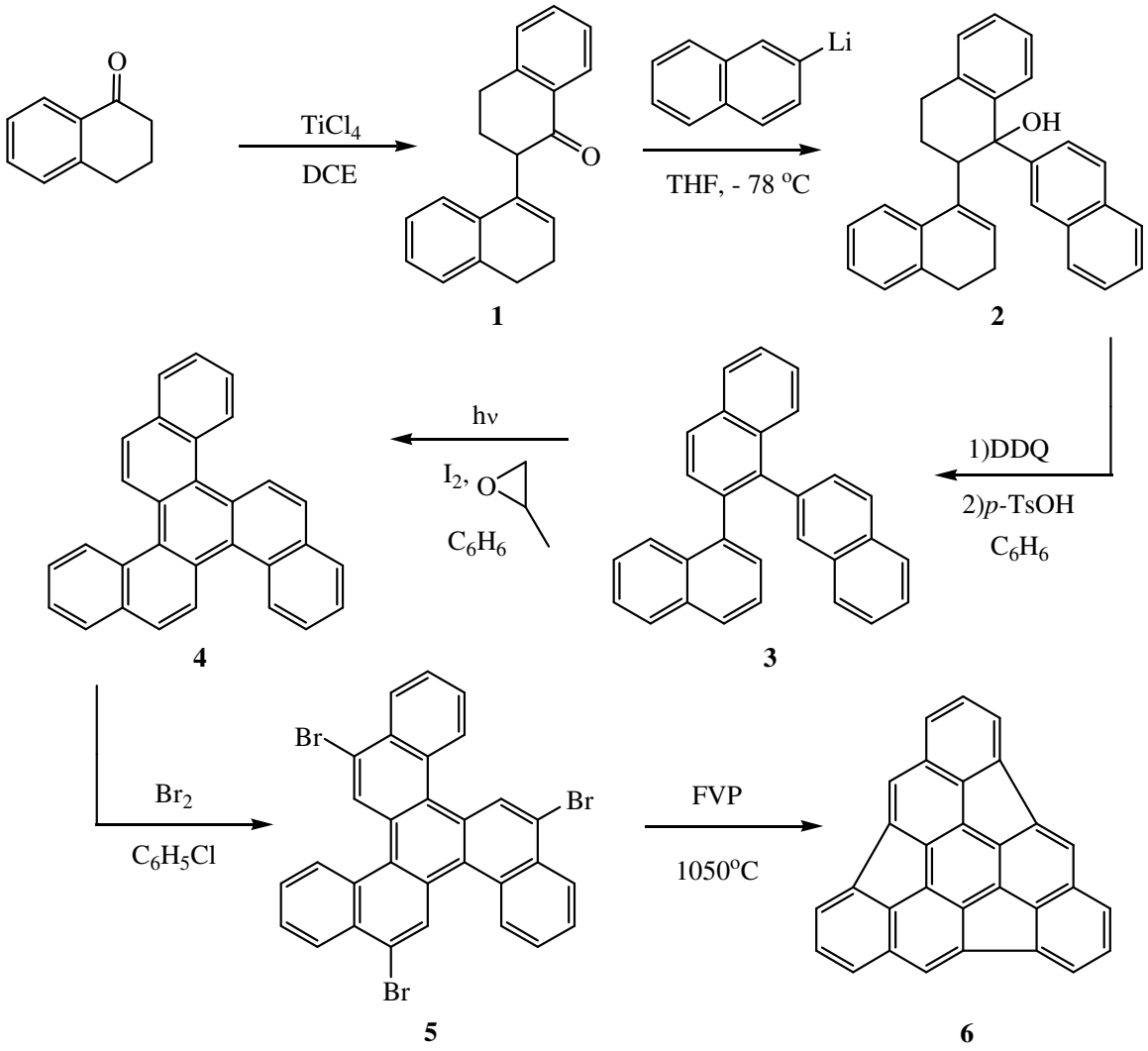


Figure 4. Synthesis of $C_{30}H_{12}$ (**6**)

The 1-tetralone was dimerized, through an aldol condensation using titanium tetrachloride as a Lewis Acid to give **1** in a 76% yield. The reaction could be run on a 50 g scale.

The 2-naphthyl lithium was produced from 2-bromonaphthalene and n-butyl lithium. To this was added **1** which afforded **2** as a white solid in yields of 86%.

Compound **2** was aromatized using DDQ and p-TsOH. The reaction could be run on a 21 g scale and produced **3** as a yellow solid in 95% yield.

The central ring of benzonaphthochrysene, **4**, was formed through a photocyclization. This reaction could be run on a 5 g scale and gave a yield of 90%.

Bromination of **4** with elemental bromine in refluxing chlorobenzene produces **5** as a yellow solid with a yield of 65%.

Flash vacuum pyrolysis of **5** at 1050 ^{o}C with a N_2 capillary gives the $C_{30}H_{12}$ bowl, **6**. The product is isolated from the crude material by column chromatography in yield of 9%.

2.5 Conclusions

This route was successfully able to produce the hemifullerene **6** in an overall yield of 4%.

2.6 Experimental

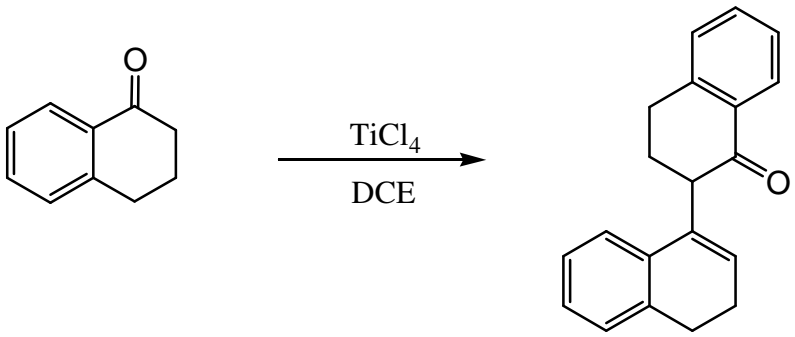
2.6.1 General

All starting materials were purchased from Aldrich chemical company and used without further purification. All solvents were used as purchased, with the exception of tetrahydrofuran, which was purified by distillation under a nitrogen atmosphere from the potassium ketyl of benzophenone prior to use.

Proton and carbon NMR spectra were generated on either a Varian 400 (400 MHz for proton, 100 MHz for carbon; FT) or a General Electric QE300 (300 MHz for proton, 75 MHz for carbon). Proton shift are recorded relative to tetramethylsilane; carbon shifts are recorded relative to dueterated chloroform. MALDI analyses were obtained on a Micromass Tof Spec2E spectrometer.

Baker 60-200 mesh silica gel or Aldrich aluminium oxide, activated, neutral, 150 mesh, surface area 155 m^2 / g, was used for column chromatography. Preparative thin layer chromatography was performed on 20 x 20 cm Analtech Uniplate Taper plates. TLC plates were purchased from J. T. Baker. For photolysis reactions a Hanovia 450 W medium pressure mercury lamp was used. All melting points were determined using a Meltemp II Melting Point Apperatus and are reported uncorrected.

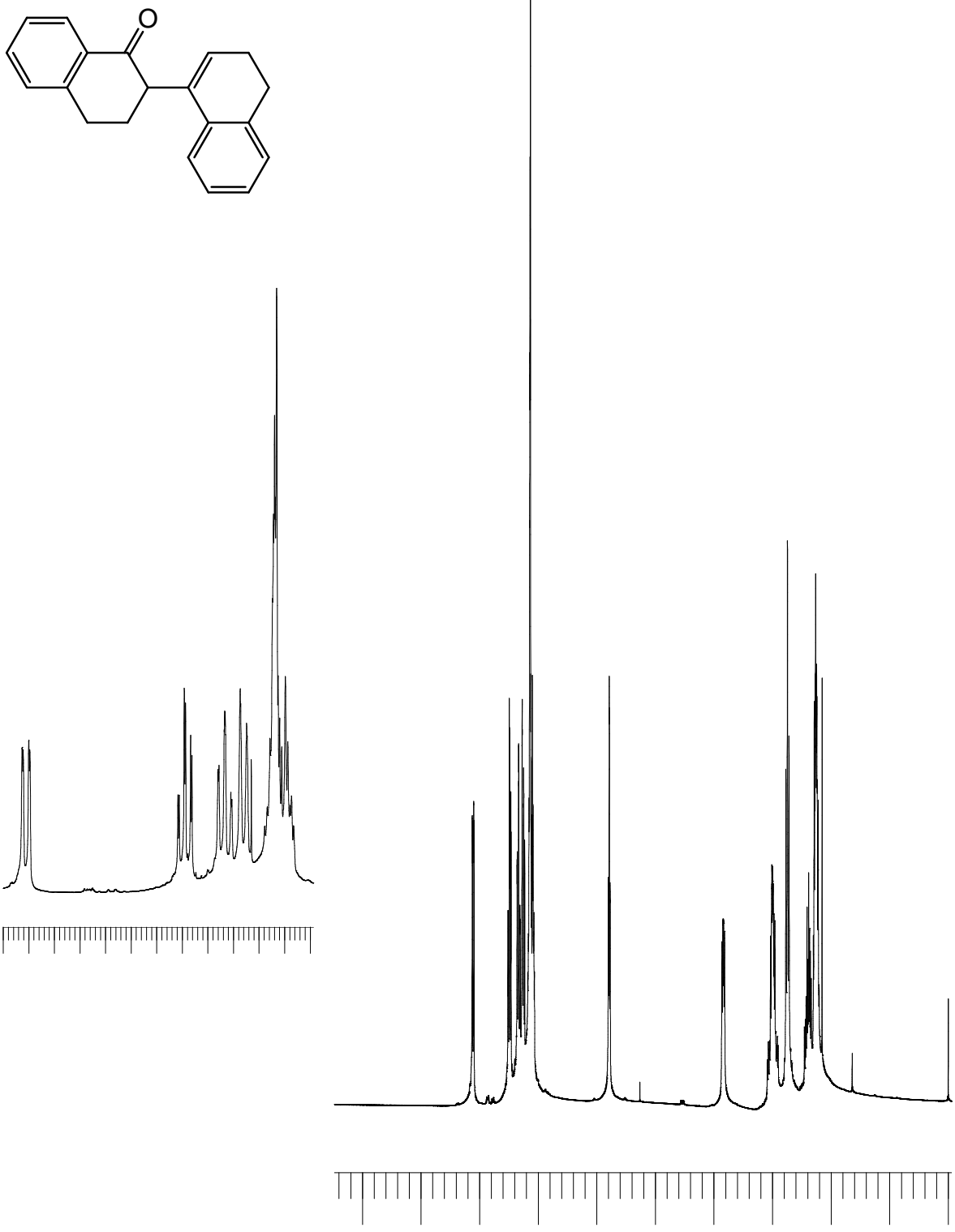
2.6.2. 3,3',4,4² Tetrahydro-[1,2'-binaphthalen]-1'(2'H)-one (1)



Into a flame dried 1 L three necked round bottom flask under nitrogen were added α-tetralone (50.0 g, 0.343 mol), and anhydrous dichloroethane (600 mL). While stirring the solution, titanium tetrachloride (25.0 mL, 0.223 mol) was added dropwise by syringe. The black solution was heated to reflux for four hours. Upon cooling to room temperature a solution of concentrated hydrochloric acid (150 mL) and ice (150 g) was added to quench the reaction mixture. This mixture was allowed to stir until the aqueous layer became fluorescent green. The product was then washed with 10% HCl solution (2 x 300 mL), water (2 x 300 mL), and brine (2 x 300 mL). The solution was dried over Magnesium sulfate and filtered. The solvent was removed, leaving a brownish-yellow oil. Recrystallization from hot ethanol gave 34.63 g (74%) of **3,3',4,4'-Tetrahydro-[1,2'-binaphthalen]-1'(2'H)-one** (**1**) as a pale yellow solid, mp 135 ^{o}C.

^{1}H NMR (300 MHz $CDCl_3$)	δ 8.12 (d, 1H, J = 7.2 Hz), 7.51 (dd, 1H, J = 7.5, 7.2 Hz), 7.35 (dd, 1H, J = 7.5, 7.2 Hz), 7.27 (d, 1H, J = 7.5 Hz), 7.20 - 7.12 (m, 2H), 7.11 – 7.06 (m, 2H), 5.90 (m, 1H), 3.85 (m, 1H), 3.01 (m, 2H), 2.75 (t, 2H, J= 7.5 Hz), 2.47 - 2.34 (m, 2H), 2.33– 2.21 (m, 2H)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 200.0, 145.0, 137.9, 136.3, 134.9, 134.4 (2C), 134.0, 129.7, 128.8, 128.6, 128.1,

127.7 (2C), 127.2, 124.1, 52.0, 30.5, 29.8, 24.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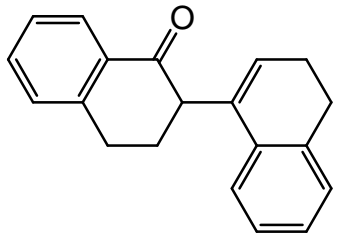
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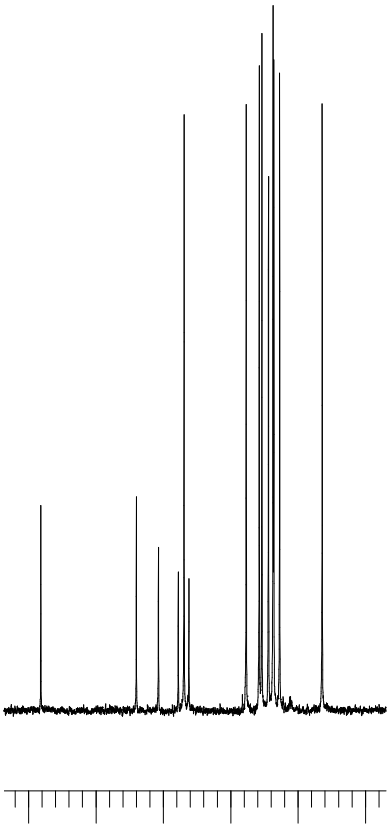
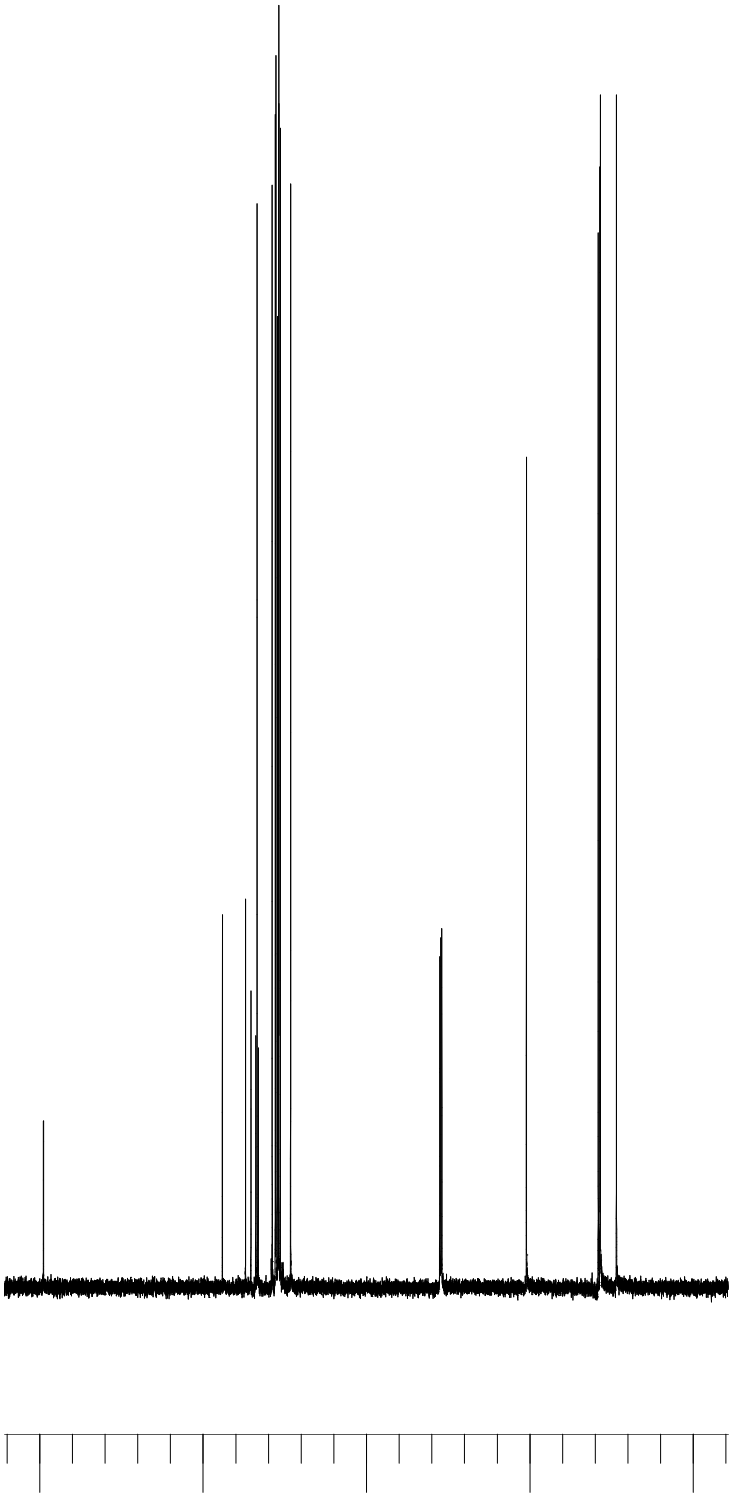
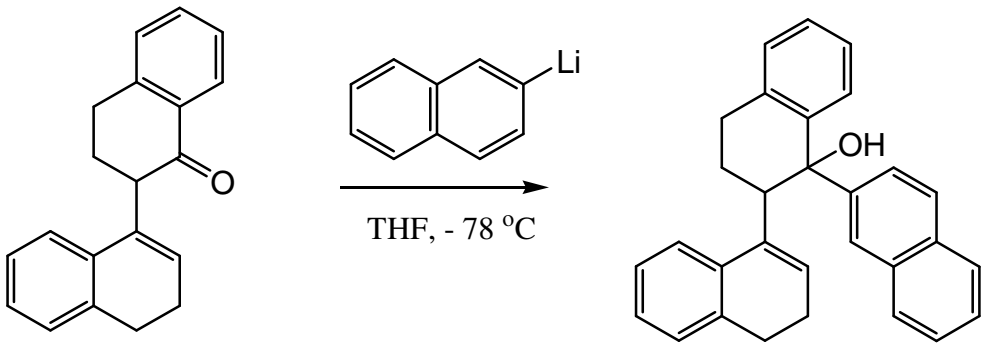


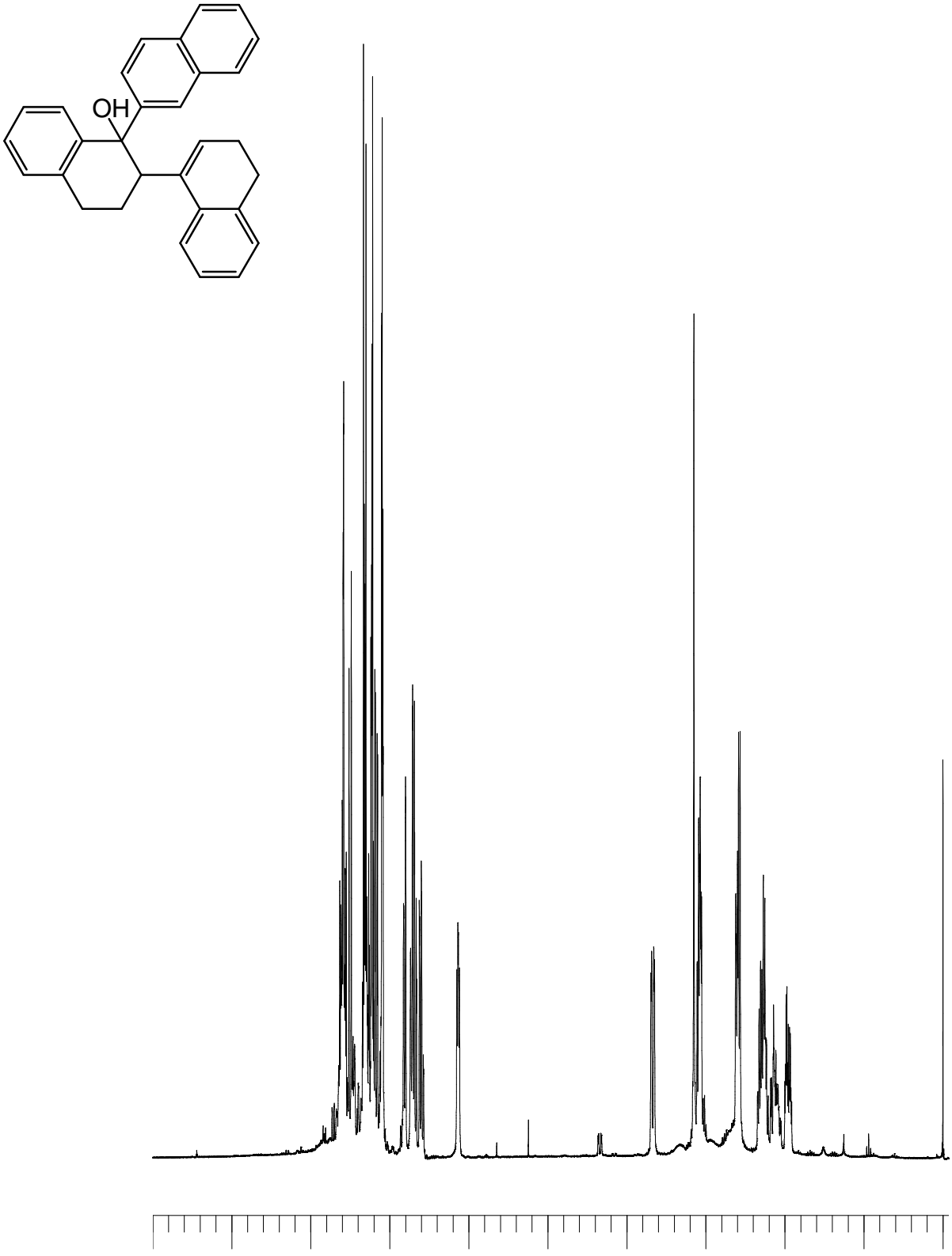


2.6.3. 3,3'4,4² Tetrahydro-[1,2':1',2''-ternaphthalen]-1'(2'H)-ol (2)



Into a flame dried 1L three necked round bottom flask under nitrogen were added 2-bromonaphthalene (18.16 g, 88 mmol) and THF (200 mL). The solution was cooled to -78 °C in a dry ice/acetone bath. While stirring, 10M *n*-butyllithium (9.8 mL, 98 mmol) was added dropwise by syringe. The solution was allowed to stir at -78 °C for 2 hr. In a 1000 mL flame dried dropping funnel under nitrogen were added a solution of **3,3',4,4'-tetrahydro-[1,2'-binaphthalen]-1'(2'H)-one** (compound **1**) (20.0 g, 73 mmol) in THF (300 mL). This solution was dropped into the 2-naphthyl litium/THF solution at -78 °C. The resulting solution was allowed to stir at -78 °C for 45 min. The solution was then warmed to room temperature and allowed to stir overnight. The solution was quenched with saturated ammonium chloride solution. Diethyl ether was added until all precipitates were dissolved. The solution was washed with ammonium chloride (2 x 300 mL), water (2 x 300 mL), and brine (2 x 300 mL). The solution was dried over magnesium sulfate and filtered. Removal of the solvent resulted in a yellow oil. Recystallization by agitating the solution in hot methanol for 30 min resulted in a white solid (20.0 g, 86%), mp 140 °C.

^{1}H NMR (300 MHz, $CDCl_3$)	δ 7.68 – 7.58 (m, 3H), 7.55 (d, 1H, J = 7.5 Hz), 7.38 – 7.33 (m, 2H), 7.28 – 7.24 (m, 2H), 7.21 (d, 1H, J = 7.2 Hz), 7.15 – 7.10 (m, 2H), 6.85 (d, 1H, J = 7.5 Hz), 6.79 -6.69 (m, 2H), 6.68 – 6.60 (m, 1H), 6.20 – 6.14 (m, 1H), 3.68 (d, 1H, J = 8.4 Hz), 3.17 (s, 1H), 3.16 – 3.00 (m, 2H), 2.64 – 2.56 (m, 2H), 2.38 – 2.23 (m, 2H), 2.22 -2.05 (m, 1H), 2.02 – 1.93 (m, 1H)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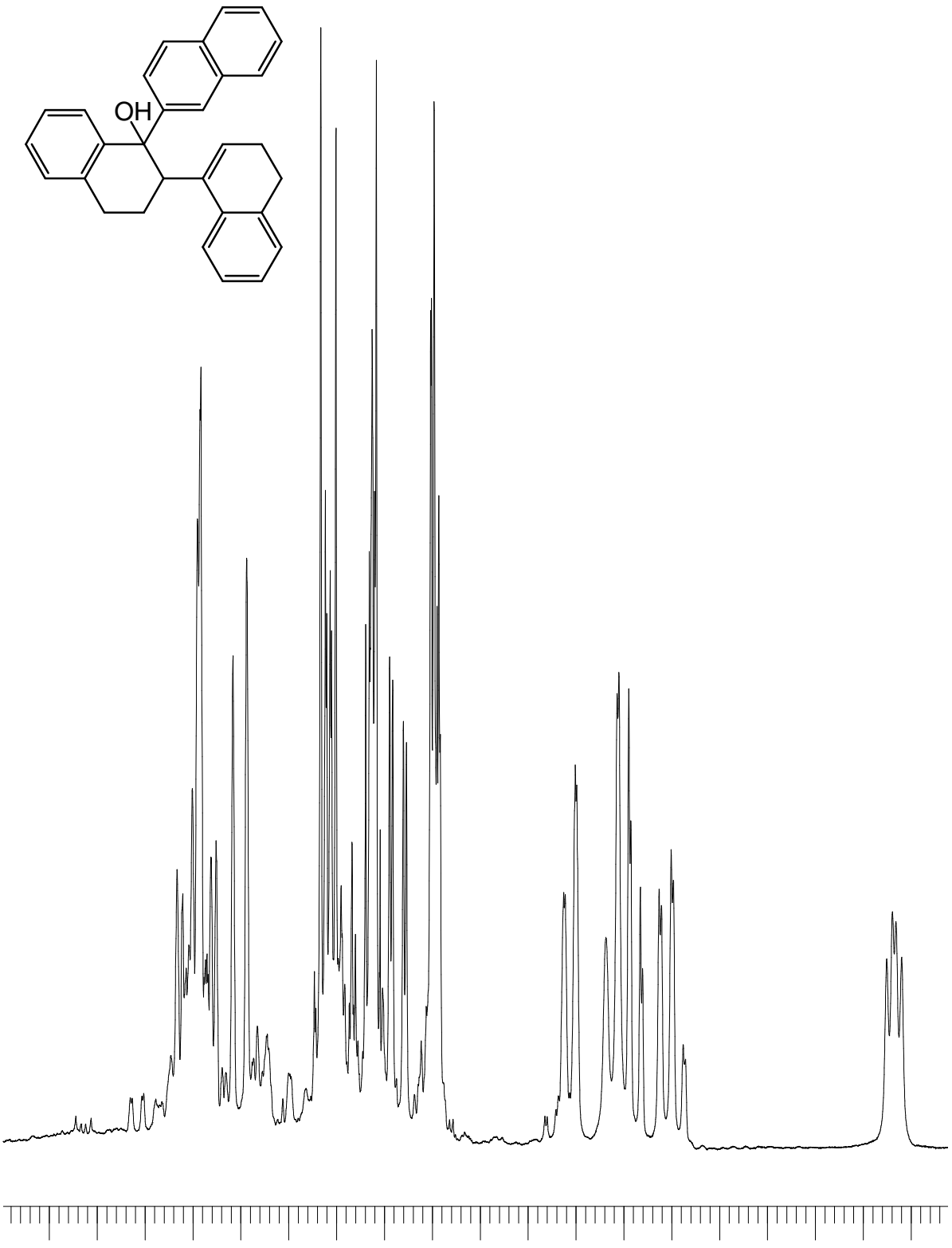
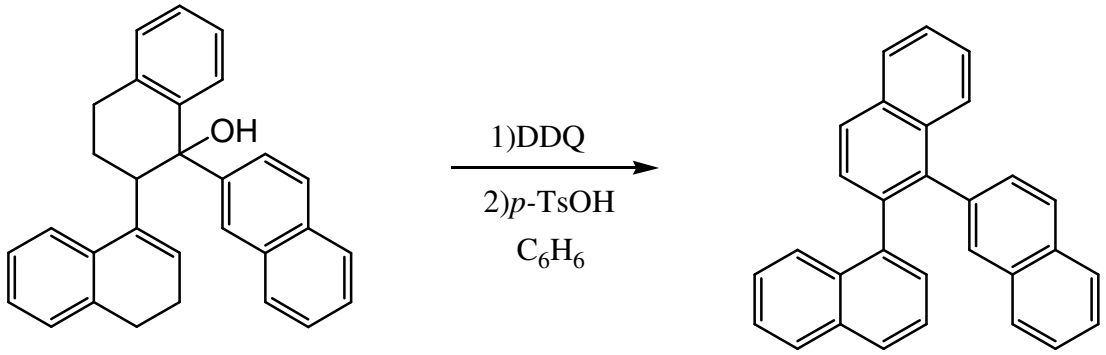
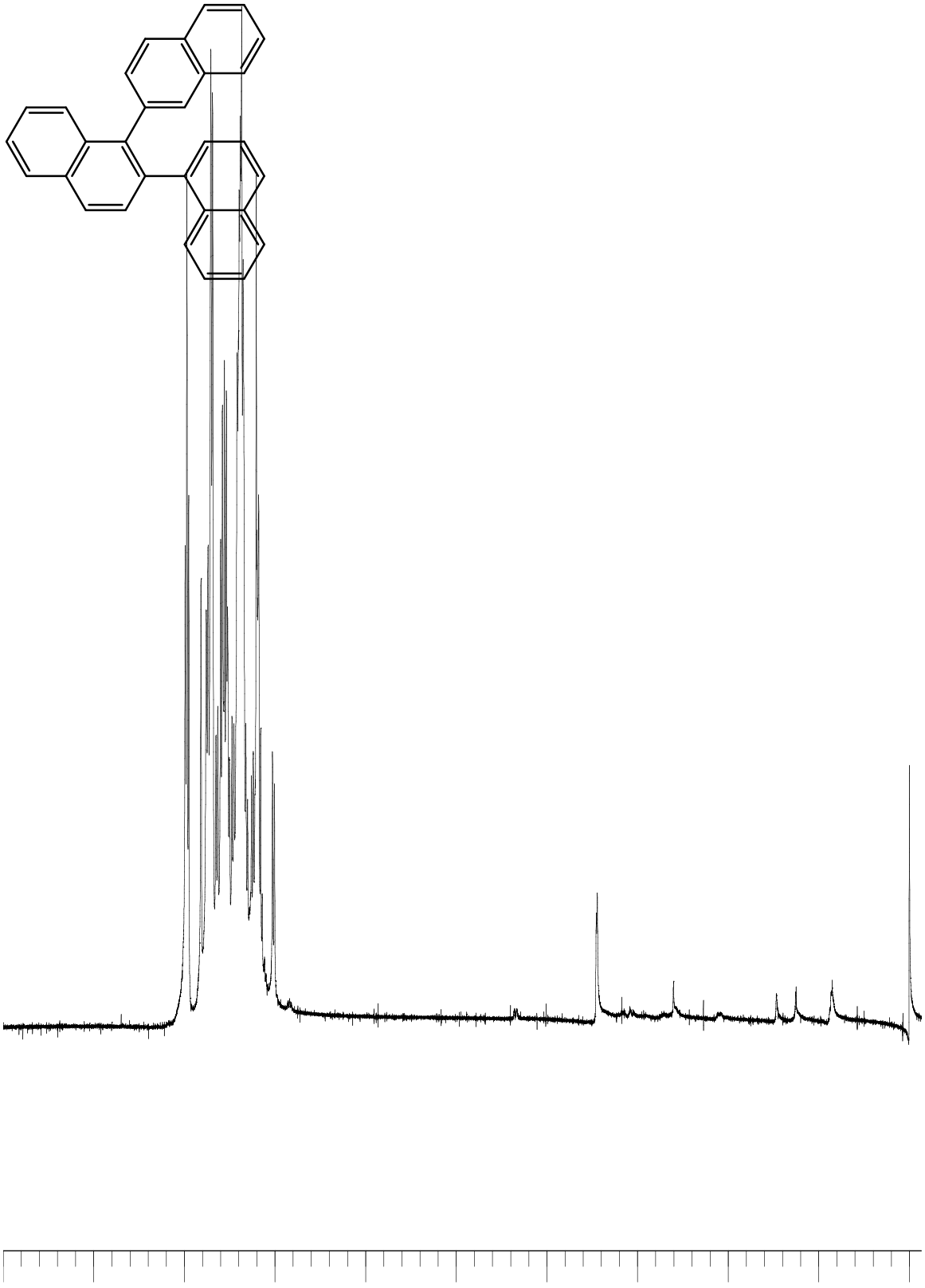

OH

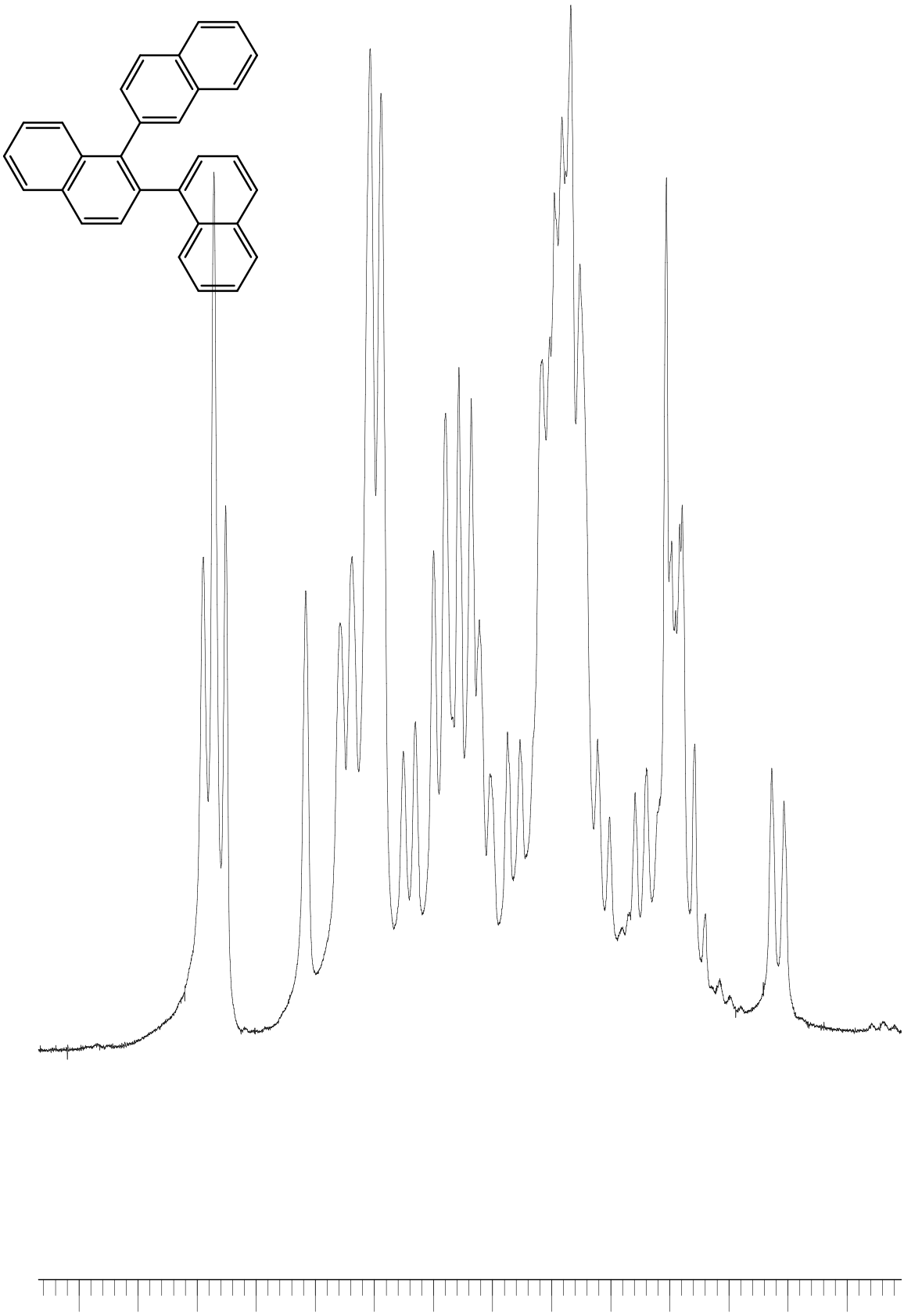
2.6.4. 1,2':1',2''-Ternaphthalene (3)



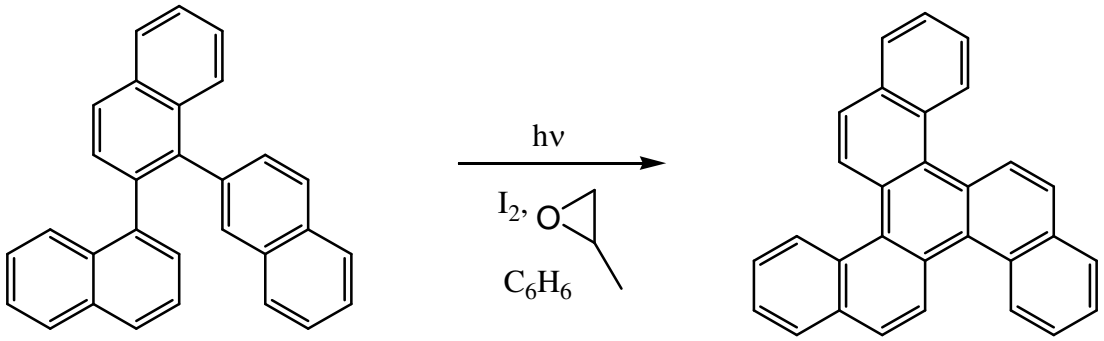
Into a 2 L three necked round bottom flask under nitrogen were added benzene (1 L) and **3,3'4,4'-tetrahydro-[1,2':1',2''-ternaphthalen]-1'(2'H)-ol** (compound **2**, 21.5 g, 54 mmol). Once the compound was dissolved, DDQ (48.6 g, 210 mmol) was added. The solution was heated to reflux for 3 hrs. To the hot solution was added 400 mg *p*-TsOH (400 mg). The solution was refluxed for an additional 2 hrs. The mixture was then cooled to room temperature. It was then flushed through a silica gel plug with benzene to remove any precipitate. The solution was then washed with 10% sodium hydroxide solution until the aqueous layer was colorless. The solution was then washed with water (2 x 500 mL) and brine (2 x 500 mL). The solvent was removed resulting in a brown oil. Recrystallization by agitating the oil in hot methanol gave 19.50 g (96%) of **1,2':1',2''-ternaphthalene (3)** as a yellow powder, mp 161 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$)	δ 8.19 - 7.98 (m, 4H), 7.97 (s, 1H), 7.86 - 7.68 (m, 8H), 7.67 – 7.58 (m, 8H), 7.56 (d, 1H, J = 7.8 Hz), 7.55 – 7.24 (m, 12H), 7.23–7.15 (m, 5H), 7.11 (d, 1H, J = 7.2 Hz) [mixture of two atropisomers]



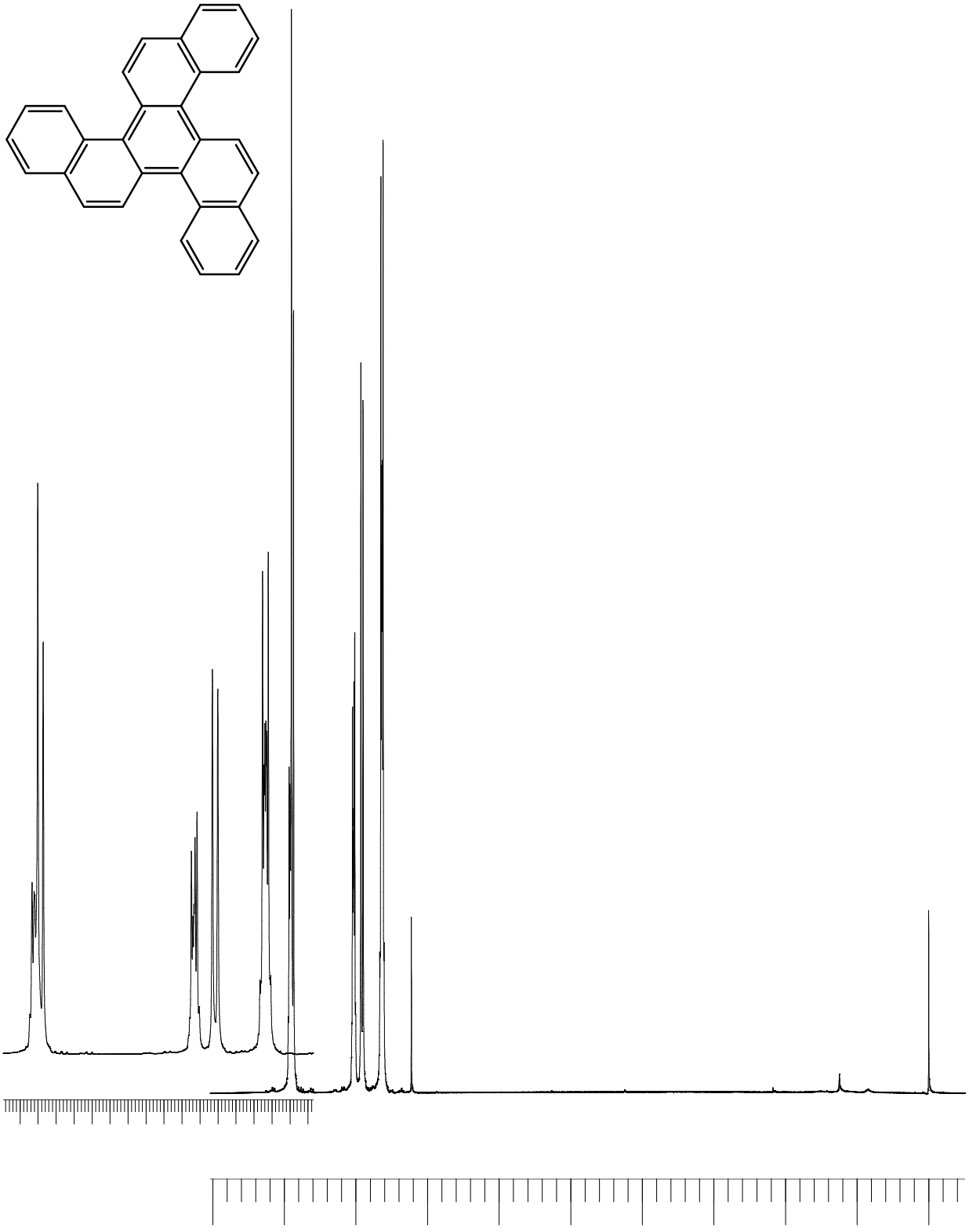


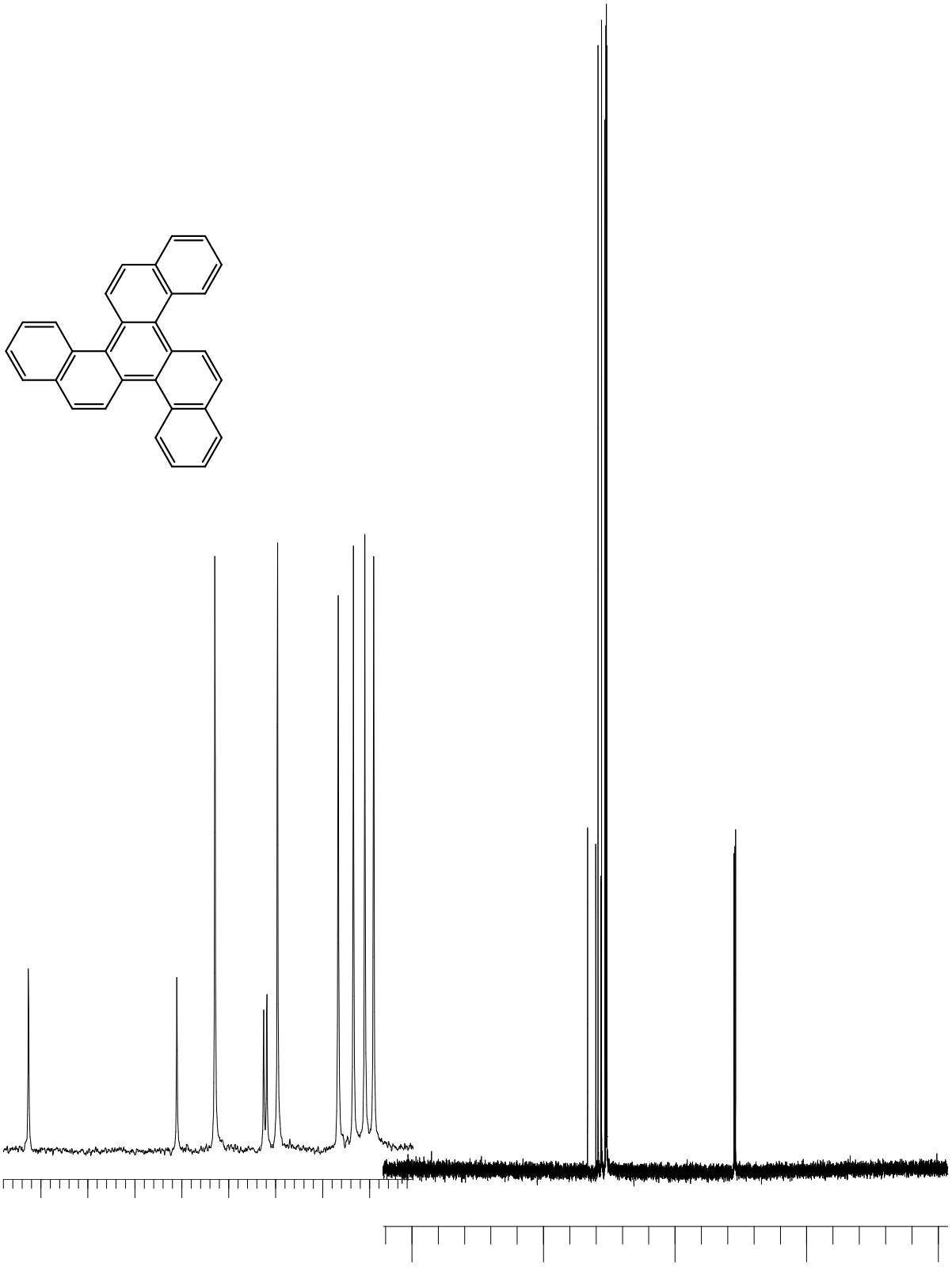
2.6.5. Benzo[c]naphtho[2,1-p]chrysene (4)



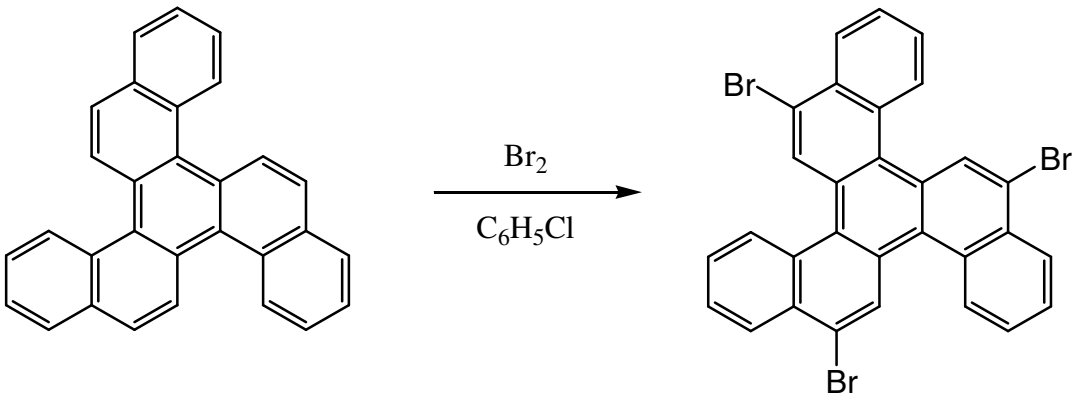
In a quartz flask were added benzene (550 mL), propylene oxide (150 mL), and **1,2':1',2''-ternaphthalene** (compound **3**) (5 g, 13 mmol). The mixture was allowed to stir until the solid was dissolved. Additionally, iodine (3.6 g, 13 mmol) was added to the solution, and the solution was purged with nitrogen for 1.5 hrs. The solution was then irradiated with a 450W medium-pressure mercury UV lamp until the solution change from a deep purple to a golden color, typically 70 – 90 hrs. Removal of the solvent resulted in an orange oil. Recrystallization in hot methanol resulted in 4.5 g (90%) **benzo[c]naphtho[2,1-p]chrysene (4)** as an orange powder, mp 235 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$)	δ 9.00 – 8.90 (m, 3H), 8.10 – 8.05 (m, 6H), 7.98 (d, 3H, 7.8 Hz), 7.74 –7.62 (m, 6H)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 133.1 (3C), 129.9 (3C), 129.1 (3C), 128.1 (3C), 128.0 (3C), 127.8 (3C), 126.5 (3C), 126.2 (3C), 125.9 (3C), 125.7 (3C)



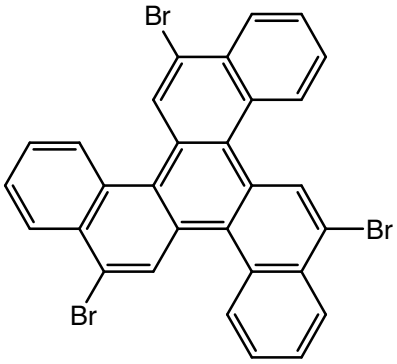


2.6.6. 6,12,18-Tribromobenzo[c]naphtho[2,1-p]chrysene (5)



Into a 360 mL round bottom pressure vessel were added 200 mL chlorobenzene and **benzo[c]naphtho[2,1-p]chrysene (4)** (5.0 g, 13 mmol). The solution was heated until all solid dissolved. The solution was then cooled to room temperature, and a solution of bromine (6.85 mL, 137 mmol) in chlorobenzene (19 mL) was added dropwise. The mixture was then heated to reflux for 1 hr. After cooling to room temperature, the yellow precipitate was collected by vacuum filtration and washed with methanol, yielding 5.25 g (65%) **6,12,18-tribromobenzo[c]naphtho[2,1-p]chrysene (5)** as a yellow powder, mp > 400 ^{o}C .

^{1}H NMR (300 MHz, $CDCl_3$)	δ 9.13 (s, 3H), 8.86 – 8.80 (m, 3H), 8.52–8.44 (m, 3H), 7.82 - 7.72 (m, 6H)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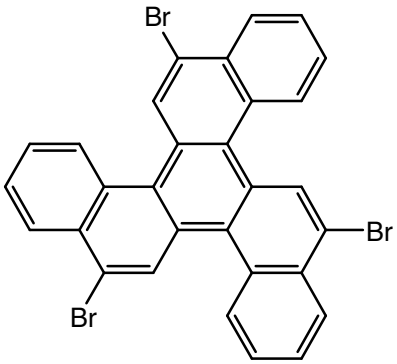
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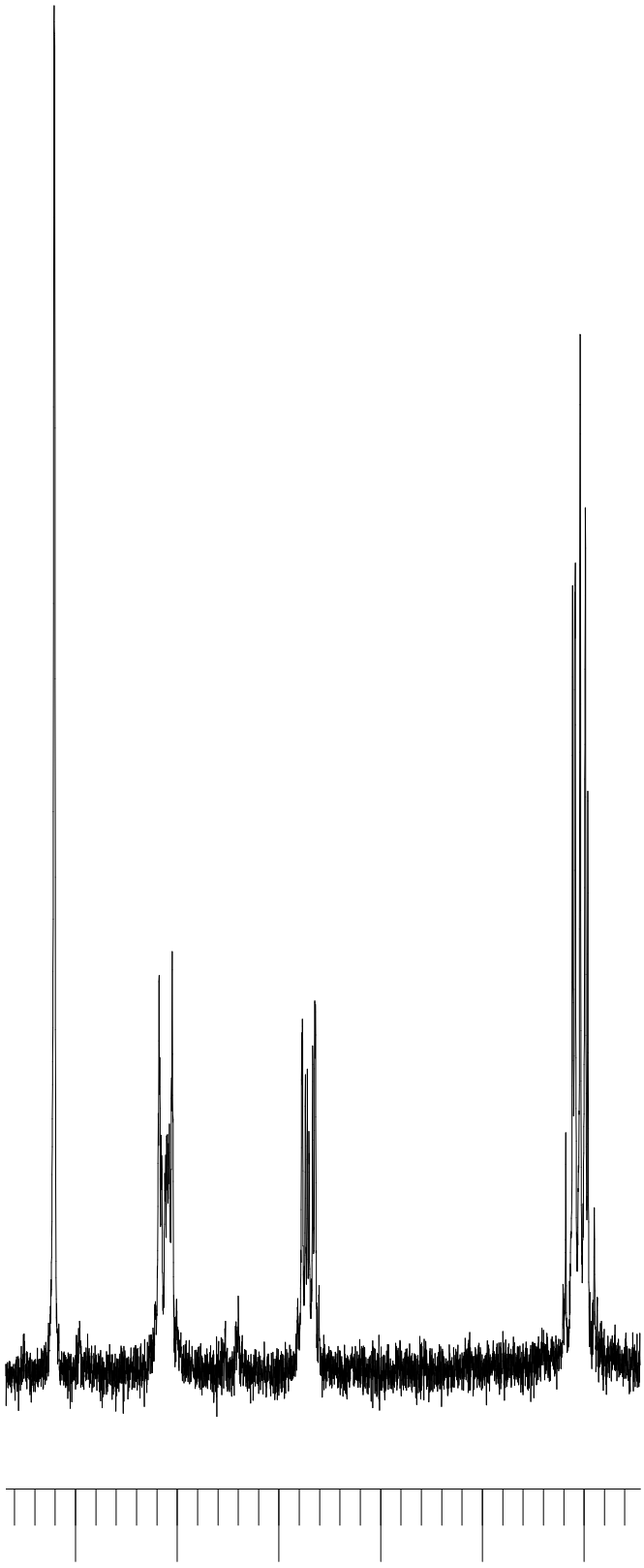
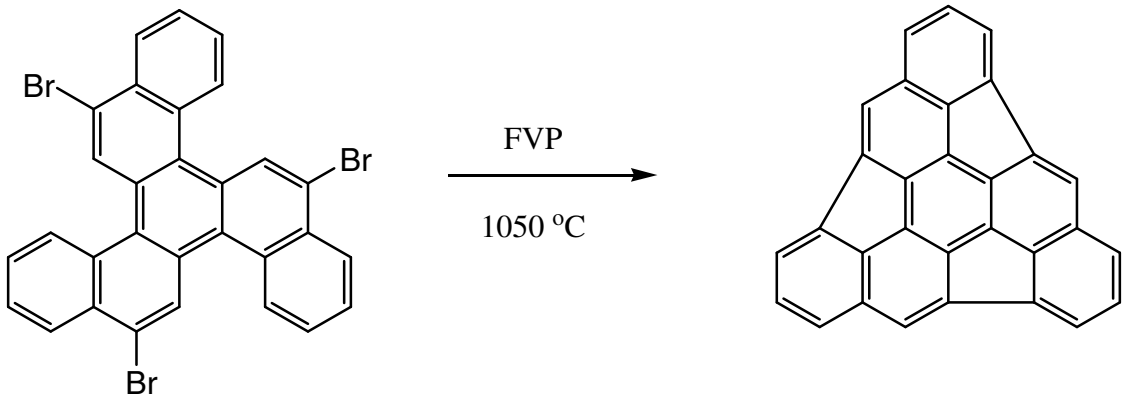
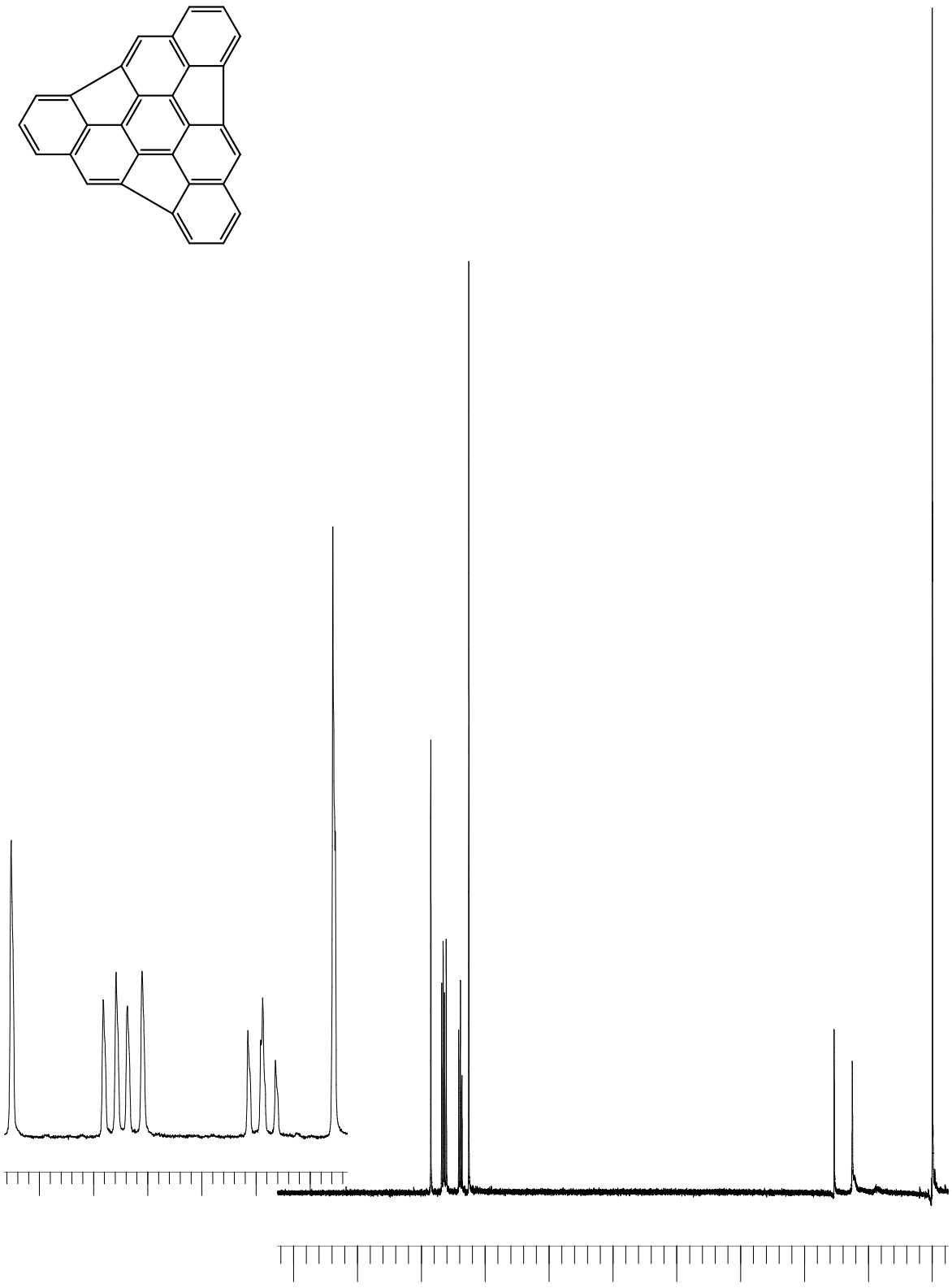


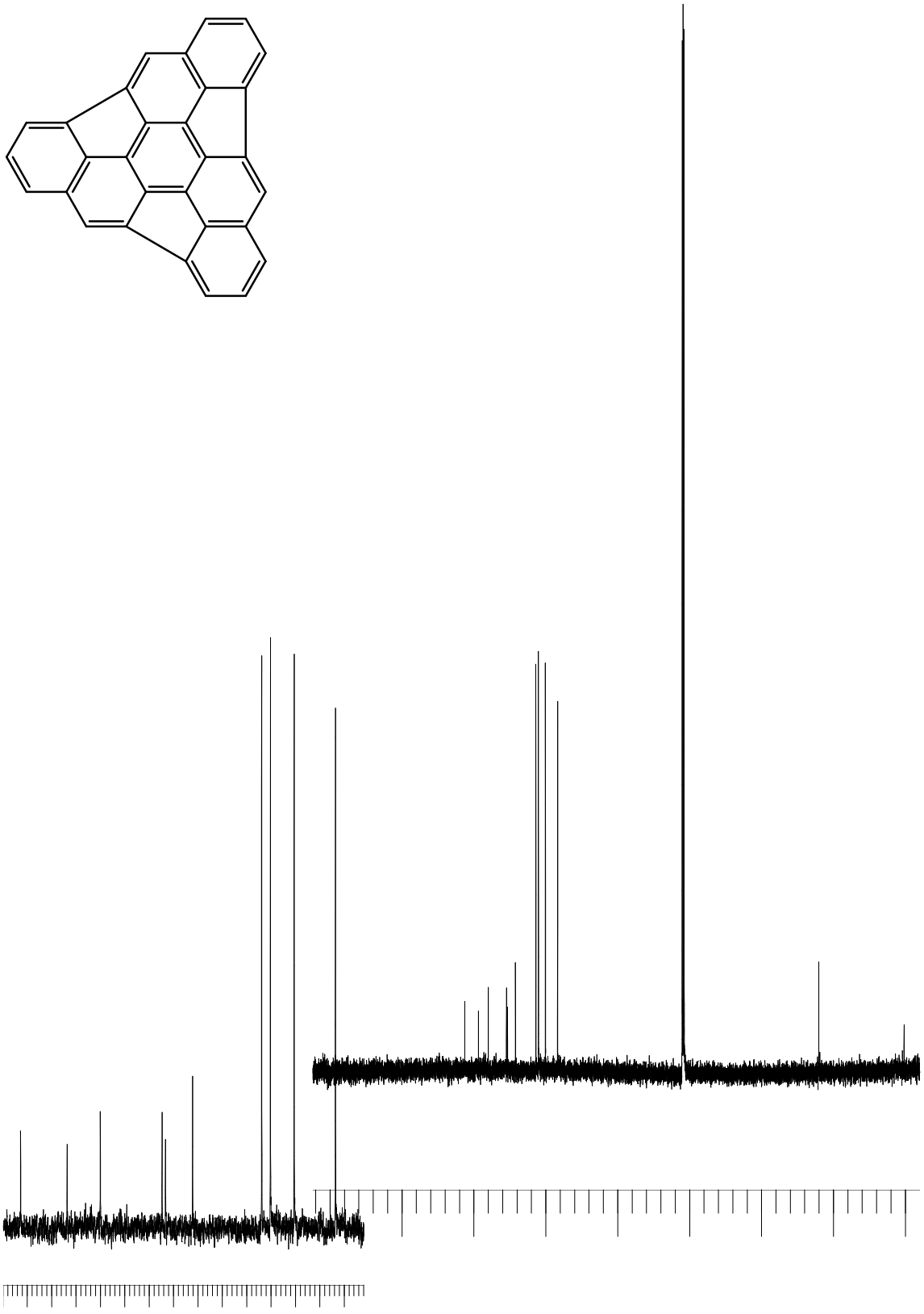
2.6.7. Benz[5,6]-*as*-indaceno[3,2,1,8,7-*mnopqr*]indeno[4,3,2,1-*cdef*]chrysene (6)



A sample of compound **5** (1.0 g) was pyrolyzed at a temperature of 1050 °C and a pressure of 0.3 mmHg. The crude product was purified by column chromatography on alumina with a 10% methylene chloride in hexanes solution as the eluent. Removal of the solvent gave 50 mg (9%) of **Benz[5,6]-*as*-indaceno[3,2,1,8,7-*mnopqr*]indeno[4,3,2,1-*cdef*]chrysene (6)** as a yellow powder, mp 354-356 °C (dec).

^{1}H NMR (300 MHz, $CDCl_3$)	δ 7.84 (s, 3H), 7.67 (d, 3H, J = 8.0 Hz), 7.62 (d, 3H, J = 8.8 Hz), 7.39 (dd, 3H, J = 8.8, 8.0 Hz)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 153.2 (3C), 148.5 (3C), 145.1 (3C), 138.7 (3C), 138.4 (3C), 135.6 (3C), 128.5 (3C), 127.6 (3C), 125.2 (3C), 121.0 (3C)





Chapter III: Alternate Route to Benzonaphthochrysene (4)

3.1 Motivation

An alternative route to benzonaphthochrysene was deemed desirable due to initial inability to scale up the photolysis step. Originally, this step could be run only on a 1 g scale and took 24 to 48 hr. Some modification was needed to scale up the reaction to its final scale of 5 g, which still requires 80-100 hrs for completion. The long duration of this reaction as well as the limited scale on which it could be run made it attractive to find an alternative route to benzonaphthochrysene which was capable of being run on large scales.

3.2 Retrosynthetic Analysis

Retrosynthetic analysis of benzonaphthochyrsene shows that the three rings attached to the central ring can be opened to form the isomer tris(ethynylphenyl)benzene, **8** (Fig. 1). This in turn can be formed by coupling commercially available tribromobenzene and (bromophenylethynyl)trimethyl silane.

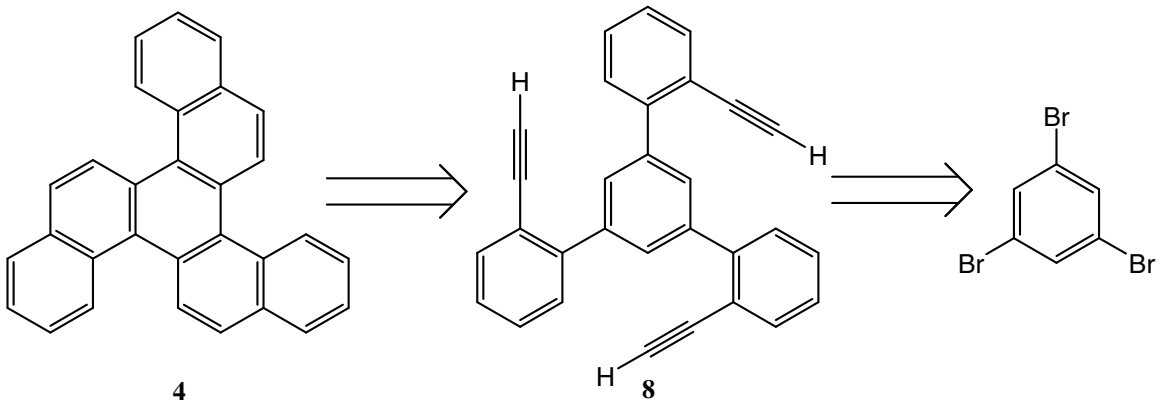


Figure 1. Retrosynthesis of Benzonaphthochrysene

3.3 Results and Discussion

This alternative synthesis of benzonaphthochrysene, **5**, requires three steps (Fig. 2).

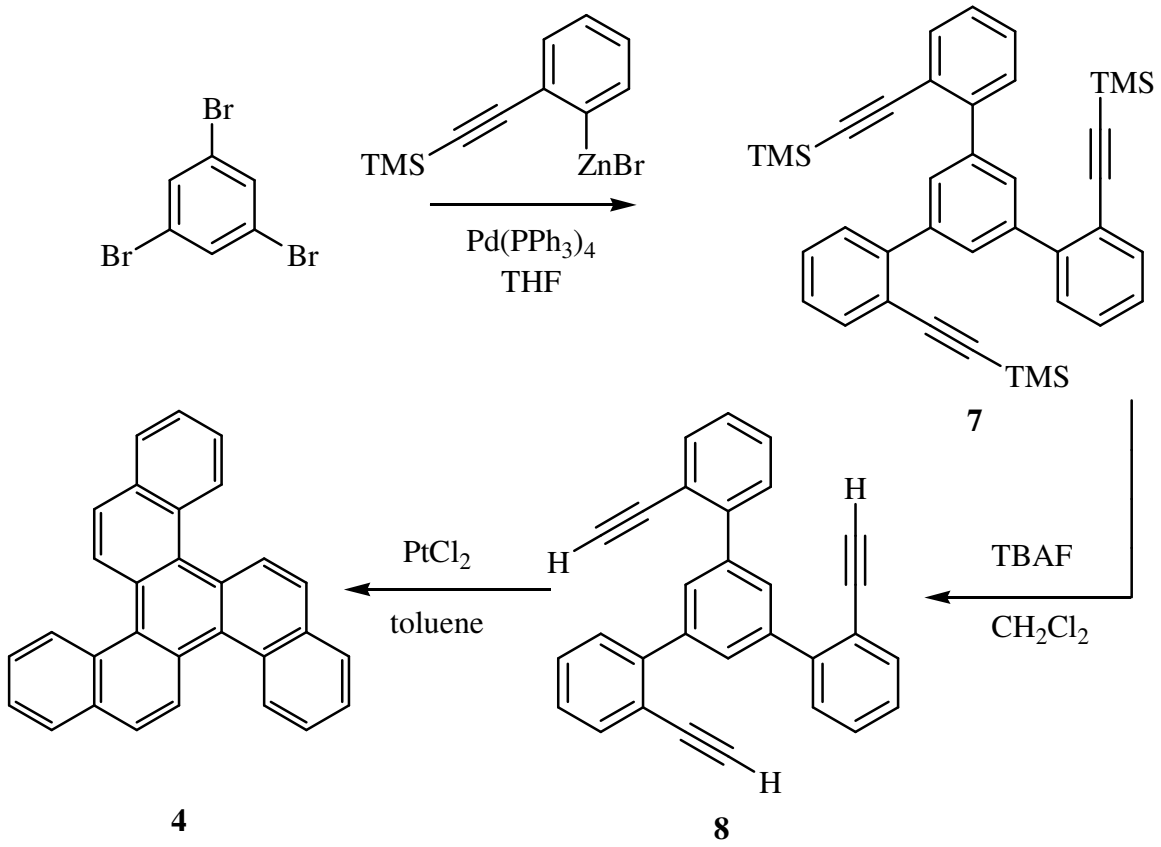


Figure 2. Alternate synthesis of benzonaphthochrysene (**5**)

Commercially available (bromophenyl)ethynyltrimethyl silane was lithiated using *n*-butyl lithium. A trans-metalation was then carried out with zinc (II) chloride to form the organozinc reagent. A palladium Negishi coupling was then performed with commercially available tribromobenzene. This reaction involved the insertion of the

palladium catalyst into the carbon-bromine bond in the tribromobenzene starting material. Alkylation by the organozinc reagent at this position produces an unsymmetrical diaryl palladium complex. Reductive elimination produces the desired product **7** and regenerates the Pd^0 catalyst. Column chromatography on the crude mixture gave product **7** as a white powder in 96% yield.

The trimethylsilyl groups of **7** were removed using tetrabutyl ammonium fluoride in dichloromethane. The reaction was performed on 2.8 g scale producing **8** as a white powder with a 91% yield.

Platinum chloride was used in an attempt to isomerize **8** to the desired benzonaphthochrysene, **4**.[9] This reaction could be done on a 0.5 g scale and produced a yield of 60%. The bromination of this product produced unexpected products. Further investigation led to the conclusion that the reaction produced polymers of **8** in addition to benzonaphthochrysene, **4**. Attempts to separate the products were unsuccessful.

3.4 Conclusions

This route was initially promising due to the fewer number of steps to benzonaphthochrysene, **4**, as well as the potential to scale up future reactions. However, this route was ultimately abandoned due to the inability to isolate pure benzonaphthochrysene, **4**.

3.5 Experimental

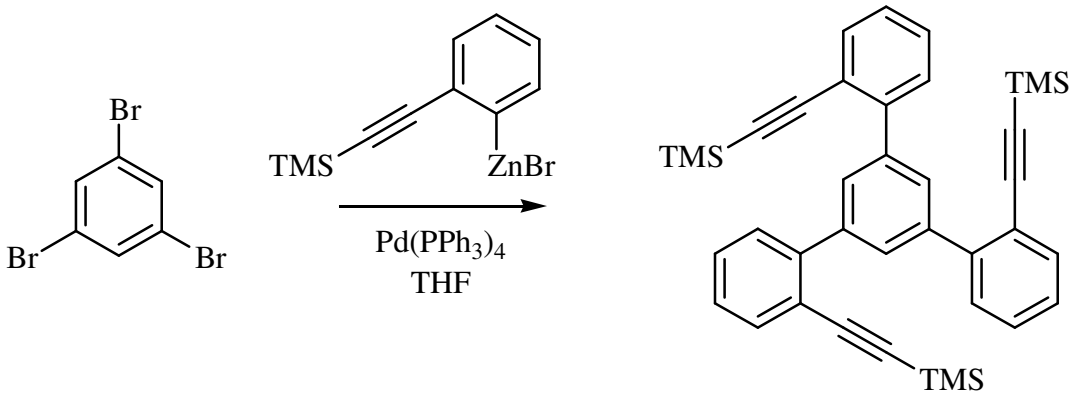
3.5.1 General

All starting materials were purchased from Aldrich chemical company and used without further purification. All solvents were used as purchased, with the exception of tetrahydrofuran, which was purified by distillation under a nitrogen atmosphere from the potassium ketyl of benzophenone prior to use.

Proton and carbon NMR spectra were generated on either a Varian 400 (400 MHz for proton, 100 MHz for carbon; FT) or a General Electric QE300 (300 MHz for proton, 75 MHz for carbon). Proton shift are recorded relative to tetramethylsilane; carbon shifts are recorded relative to dueterated chloroform. MALDI analyses were obtained on a Micromass Tof Spec2E spectrometer.

Baker 60-200 mesh silica gel or Aldrich aluminium oxide, activated, neutral, 150 mesh, surface area 155 m^2 / g, was used for column chromatography. Preparative thin layer chromatography was performed on 20 x 20 cm Analtech Uniplate Taper plates. TLC plates were purchased from J. T. Baker. For photolysis reactions a Hanovia 450 W medium pressure mercury lamp was used. All melting points were determined using a Meltemp II Melting Point Apperatus and are reported uncorrected.

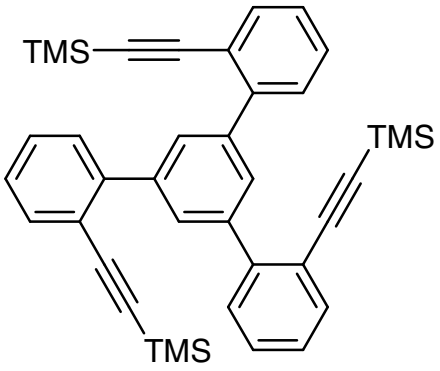
3.5.2. 1,3,5-Tris-(2-trimethylsilylethynylphenyl)-benzene (7)



Into a flame dried 50 mL three neck round bottom flask under argon were added (2-bromophenylethynyl)-trimethyl silane (2.81 g, 11.1 mmol) and 20 mL anhydrous THF by syringe. The solution was frozen-degassed three times. 1.6 M n-butyllithium (7.3 mL, 12 mmol) solution was added dropwise by syringe. The solution was stirred for 15 min at -78 ^{o}C. The solution was then checked by GC-MS to ensure all the (2-bromophenylethynyl)-trimethyl silane was consumed. A 0.500 M $ZnCl_2$ in anhydrous THF solution (24.4 mL, 12.2 mmol) was added by syringe at -78 ^{o}C and the solution was stirred for 5 min then warmed to 0 ^{o}C and stirred for an additional 30 min. In a separate flame dried 100 mL round bottom flask under argon were added 1,3,5 – tribromobenzene (0.800 g, 2.54 mmol) and tetrakis(triphenylphosphine)palladium (0.44 g, 0.38 mmol). Anhydrous THF (20 mL) was added by syringe, and the solution was frozen-degassed three times. The solution containing the fresh organozinc solution was transferred to the flask by cannula and refluxed overnight. The solution was cooled to room temperature and quenched with 10 % HCl solution and extracted with ether (25 mL). The solution was then washed with 10 % HCl solution (2 x 25 mL), water (2 x 25 mL), and brine (2 x

25 mL). All solvents were removed under vacuum, and the crude product was purified by column chromatography on silica. Compound **7** was eluted with a 10% diethyl ether / hexane solution as the eluent. Removal of the solvent under vacuum gave 1.45 g (96 %) **1,3,5-tris-2-(trimethylsilylethynylphenyl)-benzene (7)** as a white powder, mp 161 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$)	δ 8.04 (s, 3H), 7.63 (d, 3H, J = 7.6 Hz), 7.57 (d, 3H, J = 7.6 Hz), 7.42 (t, 3H, J = 7.6 Hz), 7.31 (t, 3H, J = 7.6 Hz). 0.002 (s, 27H)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 144.3 (3H), 139.6 (3H), 134.0 (3H), 129.9 (3H), 129.4 (3H), 129.1 (3H), 127.2 (3H), 120.6 (3H), 83.6 (3H), 80.7 (3H)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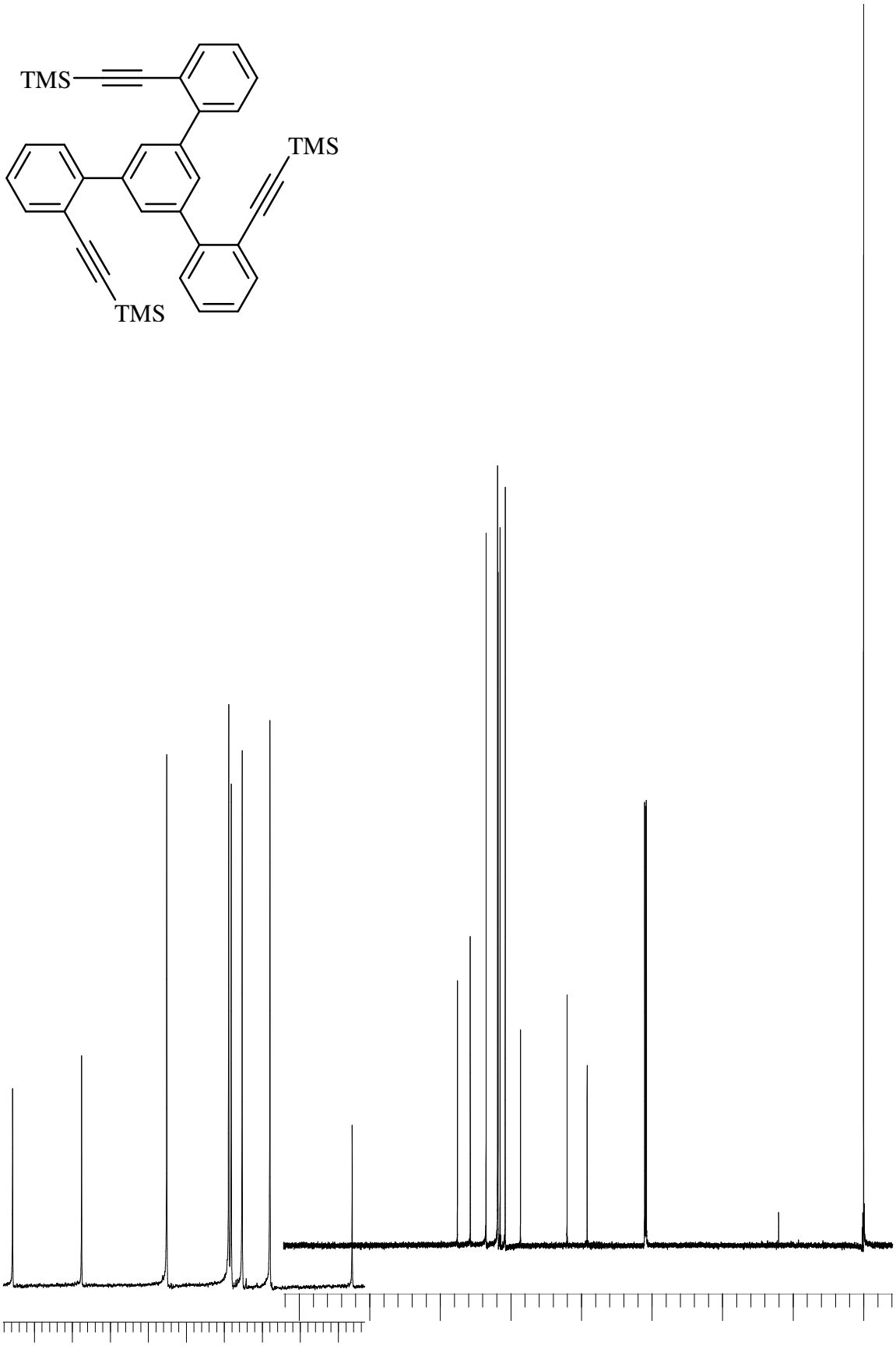
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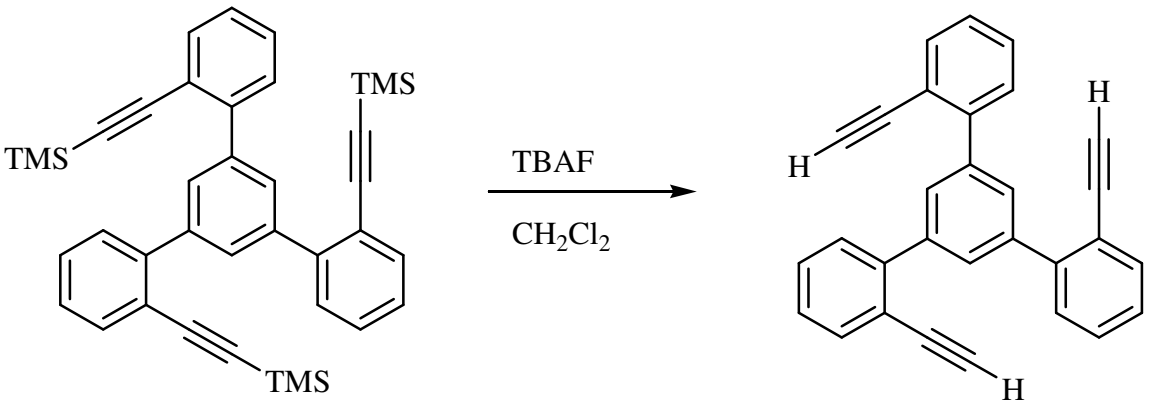
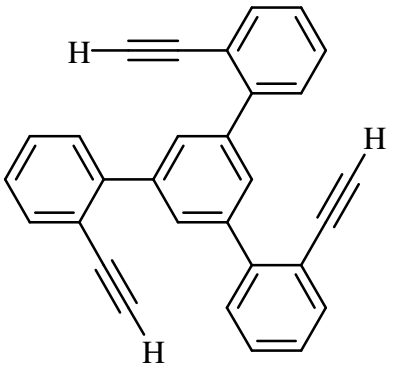
3.5.3. 1,3,5-(Tris-2-ethynylphenyl)-benzene (8)



Into a 100 mL three-neck flask were added compound **7** (2.83 g, 4.76 mmol) and dichloromethane (20 mL). A solution of tetrabutylammonium fluoride (5.99 g, 19.0 mmol) in dichloromethane (6 mL) was added to the flask dropwise at 0 ^{o}C and allowed to stir for 30 min. The solution was then quenched with methanol. It was washed with saturated ammonium chloride solution (2 x 20 mL) and water (2 x 20 mL) then dried over magnesium sulfate and filtered. The solvent was removed under vacuum and the crude product was recrystalized from methanol yielding 1.62 g (91 %) **1,3,5-(tris-2-ethynylphenyl)-benzene (8)** as a white powder, mp 119 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.85 (s, 3H), 7.63 (dd, 3H, J = 8.0, 1.2 Hz), 7.49 (dd, 3H, J = 7.6, 1,2 Hz), 7.40 (td, 3H, J = 7.5, 1.6 Hz), 7.29 (td, 3H, J = 7.5, 1.6 Hz), 3.08 (s, 3H)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 144.3 (3H), 139.6 (3H), 134.0 (3H), 129.8 (3H), 129.4 (3H), 129.1 (3H), 127.2 (3H), 120.6 (3H), 83.5 (3H), 80.7 (3H)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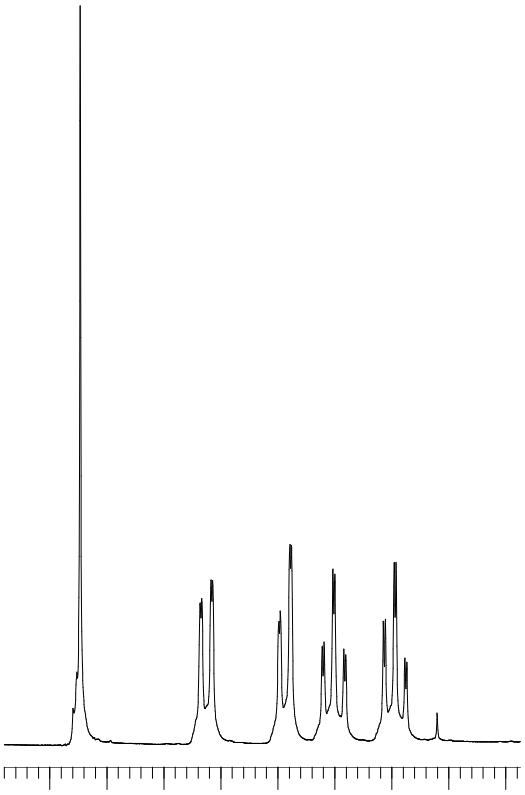

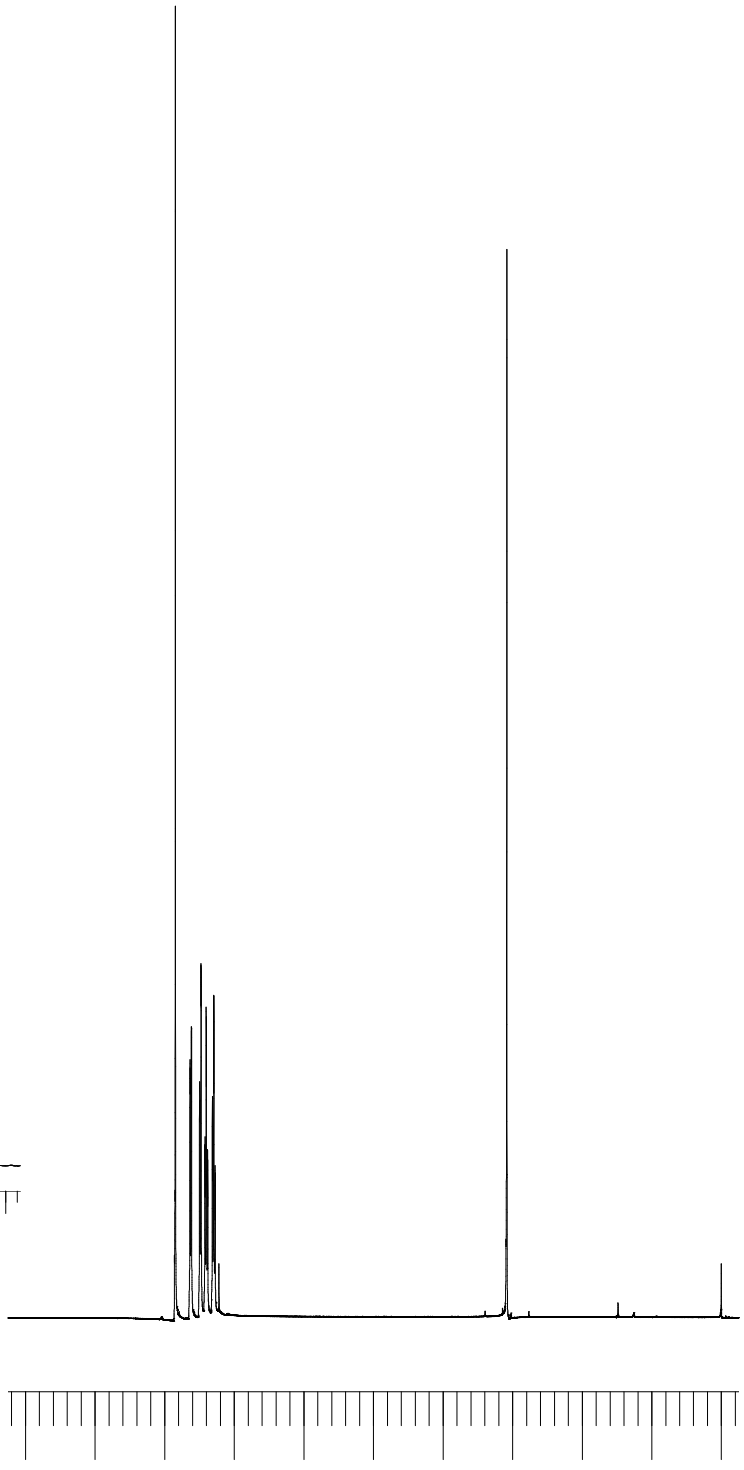

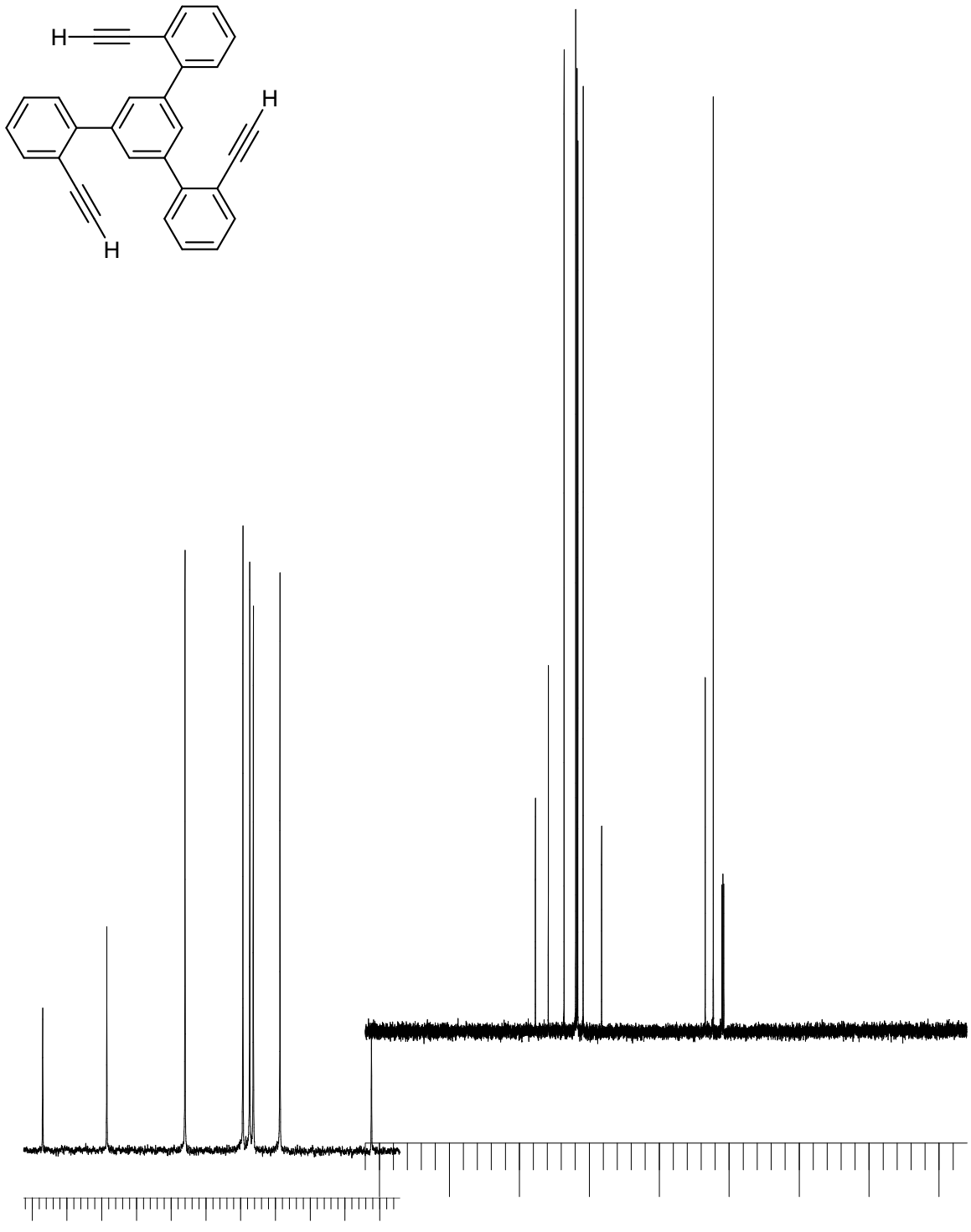
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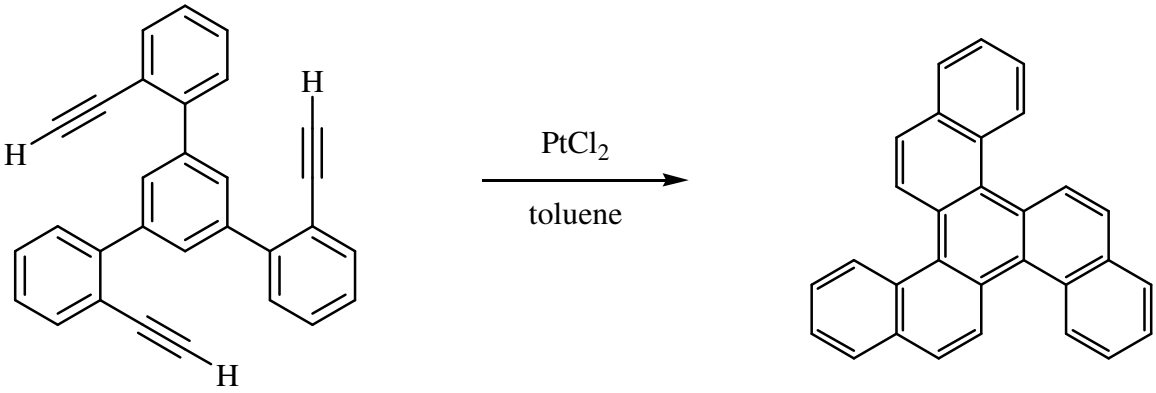
3.5.4. Benzo[c]naphtho[2,1-p]chrysene (4)



In a flame dried 50 mL two neck flask under nitrogen were added compound 8 (0.5 g, 1.32 mmol) and platinum (II) chloride (53 mg, 0.20 mmol). Toluene (25 mL) was added by syringe. The solution was heated to 100 ^{o}C overnight. The solution was cooled and washed with water (2 x 25 mL) and brine (2 x 25 mL). The solution was then dried over magnesium sulfate, filtered, and washed through a silica pad. The solvent was removed under vacuum and the crude product was recrystalized from methanol yielding 0.3 g product (60% yield). Attempts to brominate the product were unsuccessful, leading to the conclusion that the product was polymeric.

Chapter IV: Cleavage of Carbon-Carbon Sigma Bonds

4.1 Motivation

Though most emphasis in organic synthesis is placed on carbon-carbon bond formation, the cleavage of carbon-carbon bonds is of interest as well. The activation of carbon-carbon bonds is useful from a synthetic stand point. In addition, the ability to easily cleave carbon-carbon bonds would provide a way to convert coal into liquid fuels. Finally, in our laboratory there is interest in opening holes in fullerenes such as C_{60} and C_{70}. As of yet, there is little literature precedent for carbon-carbon sigma bond cleavage in hydrocarbons, though interest in this topic continues to grow.

Our strategy is to design reaction conditions using various transition metals complexes that are effective at cleaving strained carbon-carbon bonds with strong sigma character, such as those found in a $C_{30}H_{12}$ hemifullerene, **6**. As the bonds in these molecules are weaker than unstrained carbon sigma bonds and because they contain the same pattern of five and six membered rings as fullerenes, they are ideal molecules to probe for the most effective reaction conditions. Once the reaction conditions are optimized, these conditions will be applied to unstrained carbon bonds, as well as to fullerenes.

4.2 Precedent for the cleavage of strained carbon-carbon bonds

While there are many examples of the opening of three and four membered rings, to our knowledge only one example of metal insertion into a strained five membered ring exists (Fig. 1). This insertion was performed on the $C_{30}H_{12}$ hemifullerene **6**.[4r]

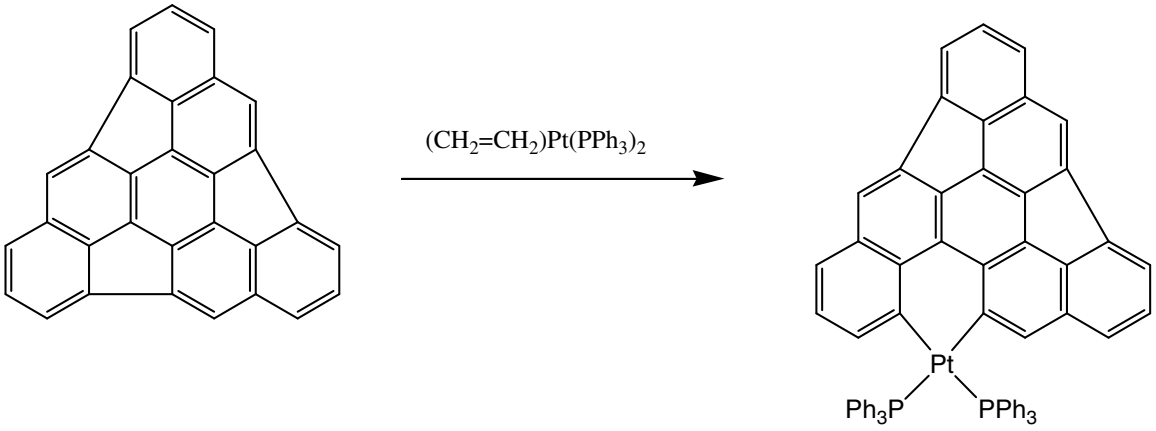


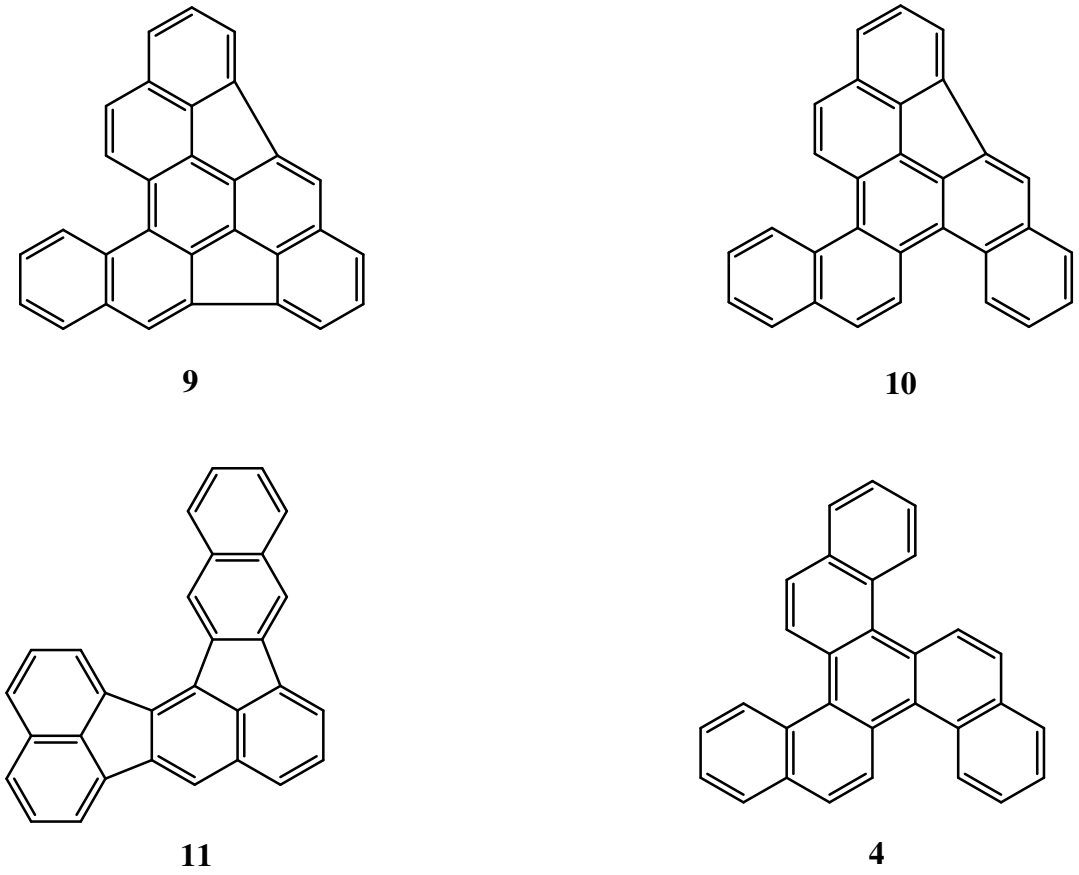
Figure 1. Platinum insertion into $C_{30}H_{12}$ hemifullerene **6**

As the ultimate goal of the project is the opening of fullerenes which contain only five and six membered rings, the $C_{30}H_{12}$ hemifullerene **6** was deemed to be an appropriate test molecule. Previous studies have shown that zero valent platinum, palladium, and nickel are effective cleavers of carbon-carbon bonds. In addition, because the insertion involves an oxidative insertion and requires open valences, the best ligands are both good electron donors and bulky. High electron density on the ligand improves HOMO-LUMO overlap between the metal and the hydrocarbon while bulky ligands prevent saturation of the metal which provides the open valences needed for carbon-carbon bond insertion.[10]

4.3 Results and Discussion

4.3.1 Energetic Considerations

As the driving force for the opening of the $C_{30}H_{12}$ hemifullerene, **6**, is the relief of strain, we wished to quantify the amount of strain that would be released from each cleavage. Four potential cleavage products were identified (Fig 2).



9 **10**

11 **4**

Figure 2. Potential carbon-carbon bond cleavage products

The total energy of each was then calculated using the B3LYP/6-31G* level of theory (Table 1).

Table 1. Calculated total energy of expected products

Compound	B3LYP/6-31G* (Hartrees)
$C_{30}H_{12}$ (**6**)	-1150.381361
$C_{30}H_{14}$ (**9**)	-1151.644121
$C_{30}H_{16}$ (**10**)	-1152.885502
$C_{30}H_{16}$ (**11**)	-1152.895670
$C_{30}H_{18}$ (**4**)	-1154.081132

The amount of strain relieved by each cleavage was then determined through a homodesmic reaction with the appropriate PAH and two benzene molecules to form biphenyl and the resulting PAH (Table 2).

Table 2. Calculated strain relieved though carbon-carbon bond cleavage

Homodesmic Reaction	E_{rxn} (kcal/mol)
$C_{30}H_{12}$ (**4**) + 2(benzene) → $C_{30}H_{14}$ (**9**) + biphenyl	-44.9
$C_{30}H_{14}$ (**9**) + 2(benzene) → $C_{30}H_{16}$ (**10**) + biphenyl	-31.5
$C_{30}H_{14}$ (**9**) + 2(benzene) → $C_{30}H_{16}$ (**11**) + biphenyl	-37.8
$C_{30}H_{16}$ (**10**) + 2(benzene) → $C_{30}H_{18}$ (**4**) + biphenyl	-2.9

These results led us to believe that the $C_{30}H_{12}$ hemifullerene, **6**, could be cleaved at least twice.

4.3.2 Cleavage of $C_{30}H_{12}$ Hemifullerene (6) with Palladium (0) Complexes

Zero valent palladium was the first metal examined in attempts to open the $C_{30}H_{12}$ hemifullerene, **6**. Four different complexes were examined bis(tri-*t*-buylphosphine) palladium, **12,** tetrakis(triphenylphospine)palladium, **13**, di(bis(di-*i*-propylphenyl) imidazole) palladium, **14,** tris(dibenzylideneacetone)dipalladium(0), **15** (Fig 4). Complexes **13** and **15** were purchased from Strem. Complex **14** was formed *in situ* from the 1,3-bis-(2,6-di-*i*-propylphenyl) imidazolium chloride and complex **15**. Complex **12** was formed from tri-*t*-butylphosphine and comple*x* **15.**

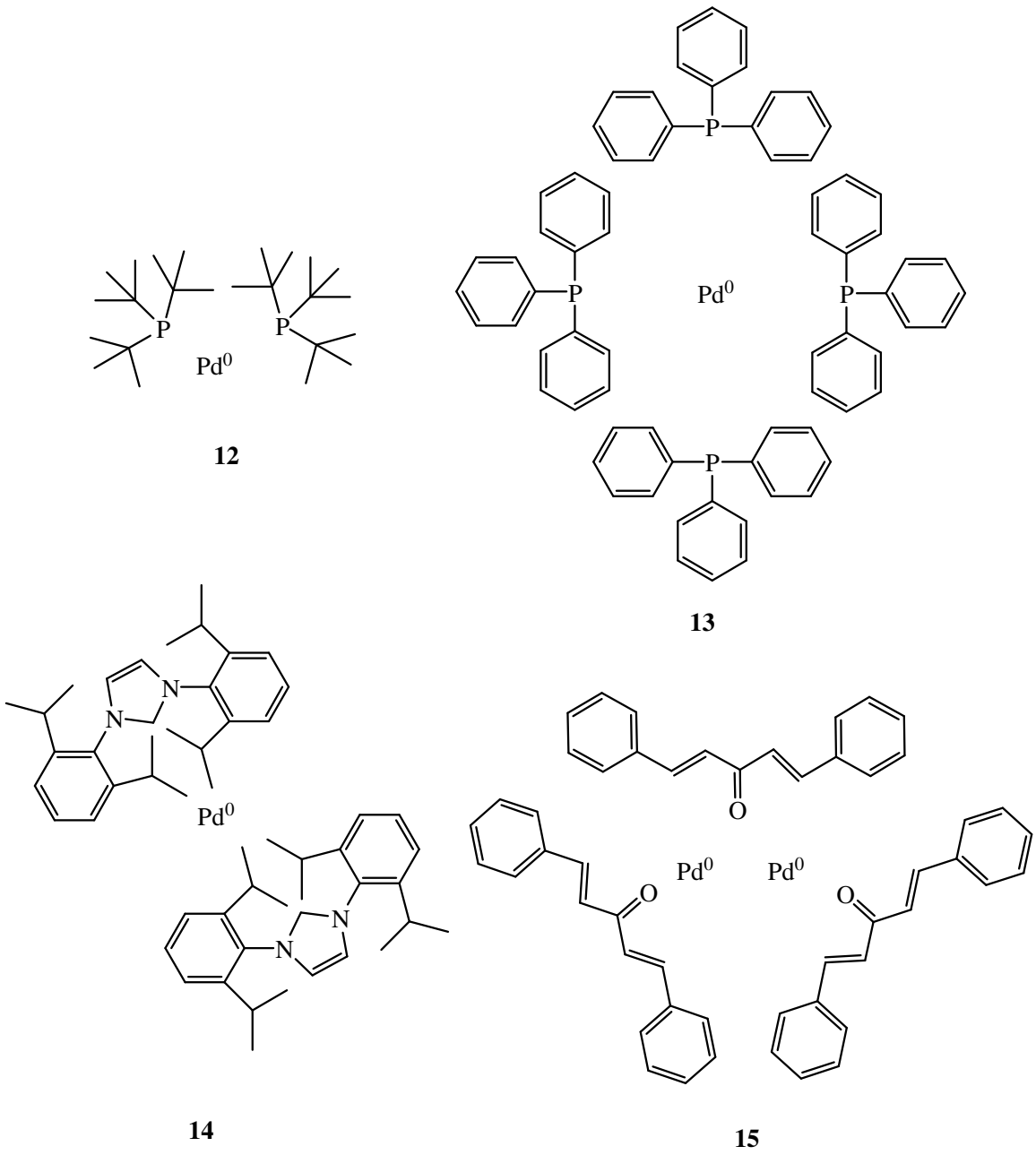


Figure 4. Zero valent palladium complexes reacted with $C_{30}H_{12}$ (**6**).

Three equivalents of each complex were reacted with $C_{30}H_{12}$ hemifullerene, **6,** at 150 ^{o}C in a sealed pressure vessel for 24 hrs in distilled THF. The crude product of each was then purified on an alumina preparative TLC plate, and the products were identified

by NMR and when necessary, MALDI. Of the four different complexes examined, the most active was complex **12** which completely converted $C_{30}H_{12}$, **6**, to $C_{30}H_{14}$, **9**. The effectiveness of this catalyst was then somewhat probed. Reaction of complex **12** with compound **6** at 100 ^{o}C for 24 hrs produced a mixture of $C_{30}H_{14}$, **9** and $C_{30}H_{12}$, **6** in a 3:4 ratio as determined by NMR integration. When the same reaction was at 150 ^{o}C for six hours it also produced a mixture of starting material and mono-opened product in a 2:1 ratio as determined by NMR. As reaction of the complex and compound **6** gave the best results, those conditions were chosen as the standard.

When complex **13** reacted with hemifullerene **6** at 150 ^{o}C for 24 hrs only starting material could be identified by NMR after purification by preparative TLC. This may be because the excess of ligand hinders reaction with **6**.

Complex **14** reacted with hemifullerene **6** at 150 ^{o}C for 24 hrs. After purification with preparative TLC only $C_{30}H_{14}$, **9** was found.

Complex **15** reacted with hemifullerene **6** at 150 ^{o}C for 24 hrs. NMR identified starting material with moderate amounts of $C_{30}H_{14}$, **9**. The ratio of **6** to **9** was determined to be 3:2 by NMR.

4.3.3 Cleavage of $C_{30}H_{12}$ Hemifullerene (6) with Nickel (0) Complexes

Four different nickel (0) complexes were reacted with the $C_{30}H_{12}$ hemifullerene, **6** (Fig 5.)**.** In each case nickel was reduced from nickel (II) to nickel (0) *in situ* using either a solution of methyl magnesium bromide or activated zinc. In each case, three equivalents of the zero valent nickel complex were used, the reaction was performed in

THF, the crude products were purified on an alumina preparative TLC plate, and the products were identified by NMR and MALDI.

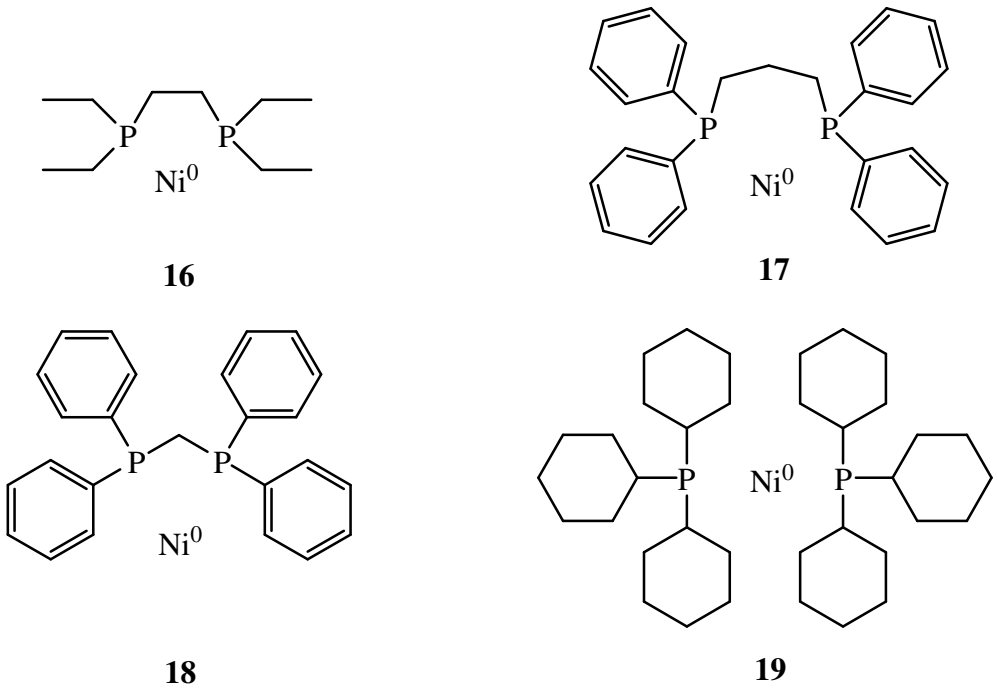


Figure 5. Zero valent nickel complexes reacted with $C_{30}H_{12}$ (**6**).

Nickel (II) acetylacetonate was stirred with the depe ligand in a solution of distilled THF to form the Ni^{II}(depe) complex. This complex was then reduced *in situ* with activated zinc (0) to form the nickel (0) complex **16**. The complex was reacted with compound **6** for 24 hrs at 150 ^{o}C. Compound **11** was obtained as the only product. After purification by preparative TLC 6.2 mg of the yellow powder was isolated from 10 mg of **6** for a yield of 62%.

Bis-(diphenylphosphino)propane nickel (II) chloride was reduced *in situ* with activated zinc (0) to form the nickel (0) complex, **17**. The zero valent complex was then reacted with hemifullerene **6** at 150 ^{o}C for 24 hrs. The major product was the mono-opened bowl **9**. The di-opened product **10** was seen in trace amounts by NMR and MALDI. The ratio of **9** to **10** was determined to be 5:1 by NMR.

The fact that three equivalents of nickel (0) complex **17** were used but only trace amounts of the di-opened bowl, **10,** were seen led to the conclusion that the catalyst was decomposing during the course of the reaction. As a result, the same reaction was run but at 100 ^{o}C for 5 days. After purification by column chromatography, 18.8 mg of compound **9** was obtained as a yellow powder from 30 mg of **6** for a yield of 63%. In addition 4.6 mg of compound **10** was obtained for a yield of 15%. Furthermore, 4.4 mg of benzonaphthochrysene was obtained for a yield of 15%. This reaction confirmed that each of the external bonds in the three five membered rings could be cleaved despite the dramatic decrease in driving force, though as with the previous reaction we suspect that the catalyst decomposes during the course of the reaction.

Complex **18** was formed *in situ* by mixing anhydrous nickel (II) acetylacetonate and dppm in a solution of distilled THF followed by a reduction with activated zinc (0). It was hoped that this complex would be more active than complex **17** as the shorter tether would make the open valences on nickel less hindered an thereby promote the oxidative addition. The zero valent complex **18** was reacted with the hemifullerene **6** for 24 hrs at 150 ^{o}C. After purification the mono-opened product was identified as the major product by NMR. The di-opened product **10** was identified as a trace product by NMR

and MALDI. The ratio of **9** to **10** was determined to be 9:1 by NMR. No starting material was detected.

A bis(tricyclohexylphosphine) nickel (II) complex was formed *in situ* from nickel (II) chloride and tricyclohexylphosphine. The complex was then reduced to the nickel (0) complex, **19,** *in situ* with activated zinc (0). Three equivalents of zero valent nickel complex was reacted with compound **6** for 24 hrs at 150 ^{o}C. The compound $C_{30}H_{14}$, **9**, was purified from the crude product mixture and identified by NMR as the only cleavage product.

4.4 Conclusions

All three of the external bonds of the five membered rings of $C_{30}H_{12}$ hemifullerene, **6** was successfully cleaved. In addition internal cleavage of the central six memebered ring was achieved using the depe ligand and nickel (0). However, these reactions were only accomplished stoichiometrically not catalytically.

4.5 Suggestions for Further Work

Stoichiometric cleavage of the carbon-carbon sigma bonds in hemifullerene **6** was accomplished, but the reaction has not yet been run catalytically. Work should be done to determine if catalytic cleavage is feasible. In addition, optimal conditions should be run on buckminsterfullerene in order to ascertain if these hydrogenolysis conditions are applicable to fullerenes.

4.6 Experimental

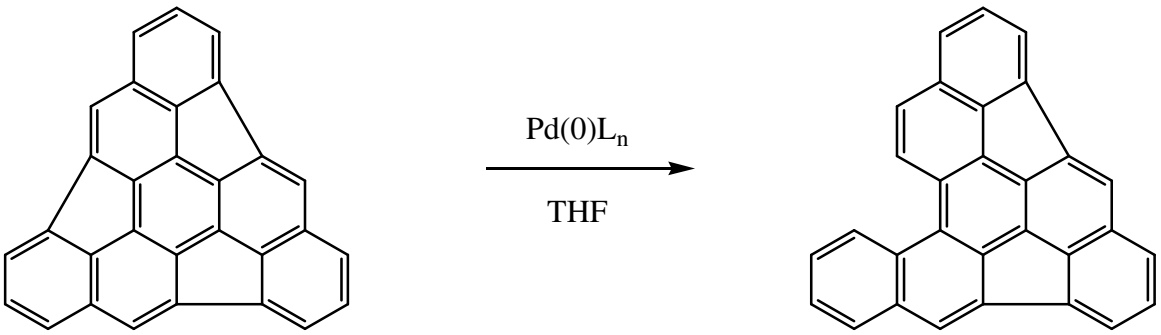
4.6.1 General

All starting materials were purchased from Strem chemical company and used without further purification. All solvents were used as purchased, with the exception of tetrahydrofuran, which was purified by distillation under a nitrogen atmosphere from the potassium ketyl of benzophenone prior to use.

Proton and carbon NMR spectra were generated on either a Varian 400 (400 MHz for proton, 100 MHz for carbon; FT) or a General Electric QE300 (300 MHz for proton, 75 MHz for carbon). Proton shift are recorded relative to tetramethylsilane; carbon shifts are recorded relative to dueterated chloroform. MALDI analyses were obtained on a Micromass Tof Spec2E spectrometer.

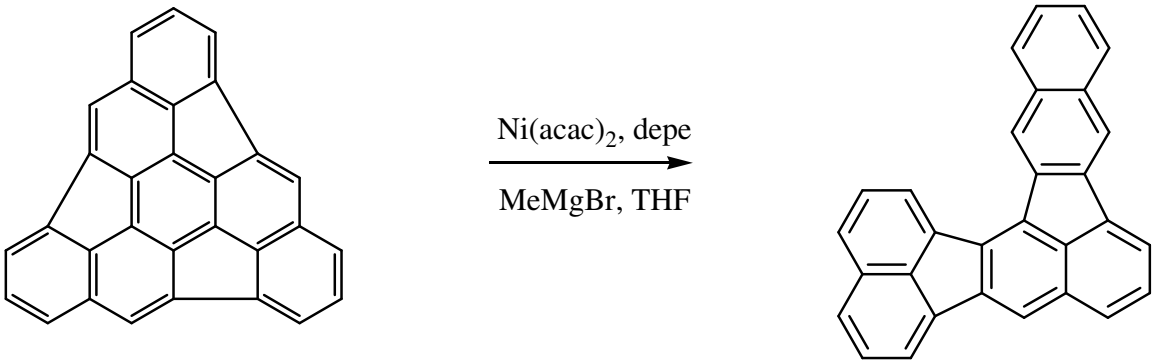
Baker 60-200 mesh silica gel or Aldrich aluminium oxide, activated, neutral, 150 mesh, surface area 155 m^2 / g, was used for column chromatography. Preparative thin layer chromatography was performed on 20 x 20 cm Analtech Uniplate Taper plates. TLC plates were purchased from J. T. Baker. For photolysis reactions a Hanovia 450 W medium pressure mercury lamp was used. All melting points were determined using a Meltemp II Melting Point Apperatus and are reported uncorrected.

4.6.2. Palladium (0) (General procedure)



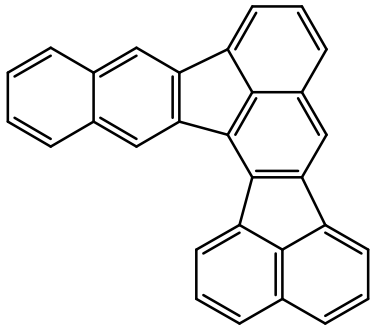
In a dry 15 mL pressure vessel under nitrogen was added the palladium (0) complex (3 eq/**6**). In the case of imidizole, $Pd_2(dba)_3$ was used as the palladium (0) source and the 1,3-di(2,6-bis(di-*i*-propylphenyl) imidazole) chloride ligand (2 eq/**6**) were added in addition to cesium (II) carbonate (3 eq/**6**). THF (3 mL) was added by syringe. The solution was frozen-degassed three times at -78 ^{o}C. Compound **6** (10 mg, 0.027 mmol) was added. The reaction was heated to 150 ^{o}C for 24 hrs. The solution was cooled and flushed through a silica plug with dichloromethane. The solvent was removed under vacuum. The crude product was purified by TLC chromatography using 5% dichloromethane / cyclohexane as the eluent. The product ratio was then determined by NMR.

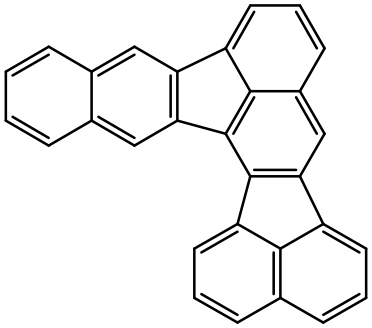
4.6.3. $C_{30}H_{16}$ (inner opening)

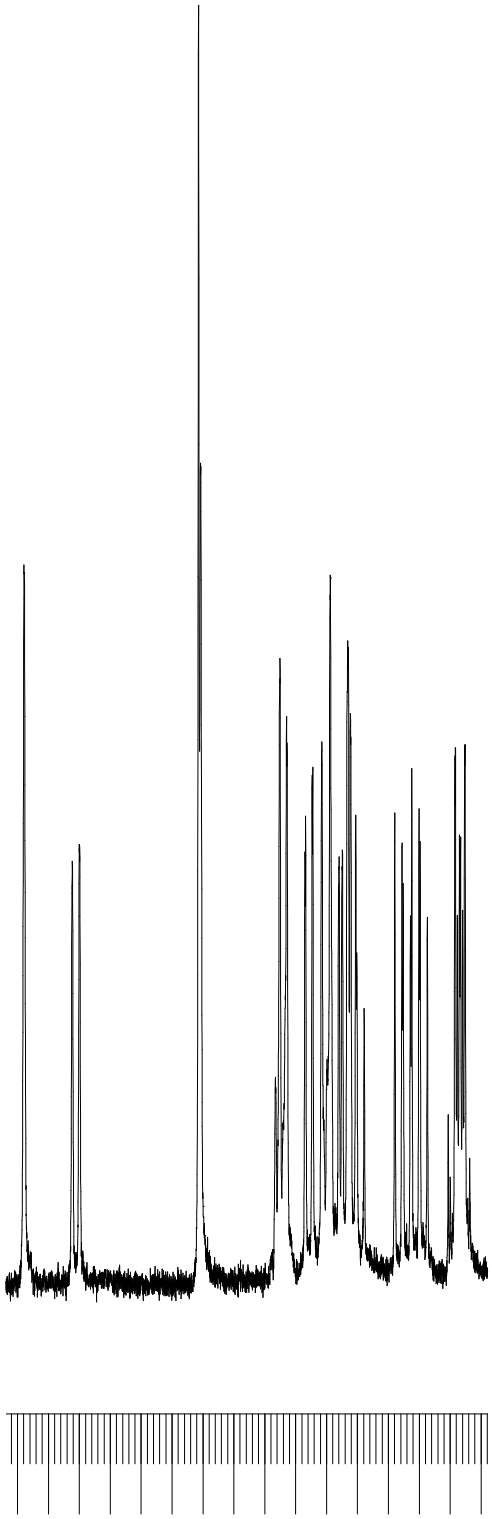


In a dry 15 mL pressure vessel under nitrogen were added Nickel(II) acetylacetonate (42 mg, 0.162 mmol), and 1,2-bis(diethylphosphino)ethane (44 μL, 0.162 mmol). THF (3 mL) was added by syringe. The solution was frozen-degassed three times at -78 °C. A 0.302 M solution of methyl magnesium bromide in THF (1.20 mL, 0.324 mmol) and compound **6** (20 mg, 0.054 mmol) were added. The reaction was heated to 150 °C for 24 hrs. The solution was cooled and flushed through a silica plug with dichloromethane. The solvent was removed under vacuum. The crude product was purified by TLC chromatography using 50% dichloromethane / cyclohexane as the eluent. The product was collected as a bright yellow powder 12.6 mg, 63% yield, mp = 265 °C.

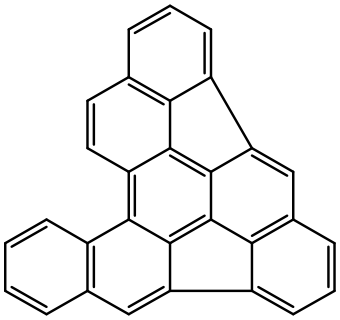
^{1}H NMR (300 MHz, $CDCl_3$)	δ 8.98 (s, 1H), 8.81 (d, 1H, J = 7.2 Hz), 8.42 (s, 1H), 8.41 (s, 1H), 8.16-8.13 (m, 2H), 8.06 (dd, 1H, J = 6.9, 0.6 Hz), 8.00 (d, 2H, J = 8.1 Hz), 7.95 (d, 1H, J = 8.7 Hz), 7.94 (d, 1H, J = 7.8 Hz) 7.90 (t, 1H, 8.7 Hz), 7.75 (dd, 1H, J = 7.2, 6.9 Hz), 7.70 (dd, 1H, J = 7.2, 6.9 Hz), 7.59-7.55 (m, 2H)

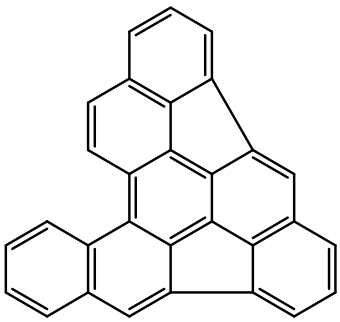


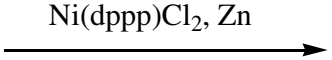


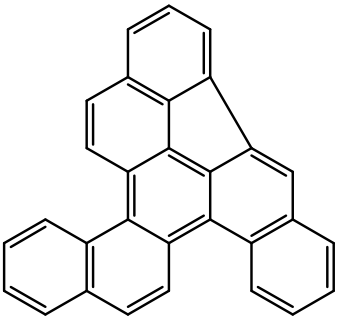


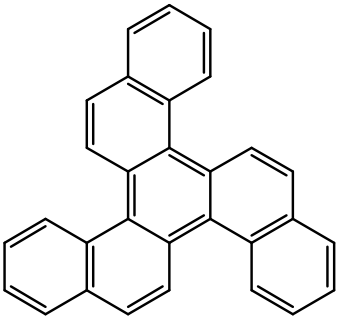
4.6.4. Ni(dppp)Cl_2











In a dry 15 mL pressure vessel under nitrogen were added [1,2-bis(diphenylphosphino) propane] nickel (II) chloride (132 mg, 0.242 mmol) and tetrabutylammonium iodide (60 mg, 0.161 mmol). THF (3 mL) was added by syringe.

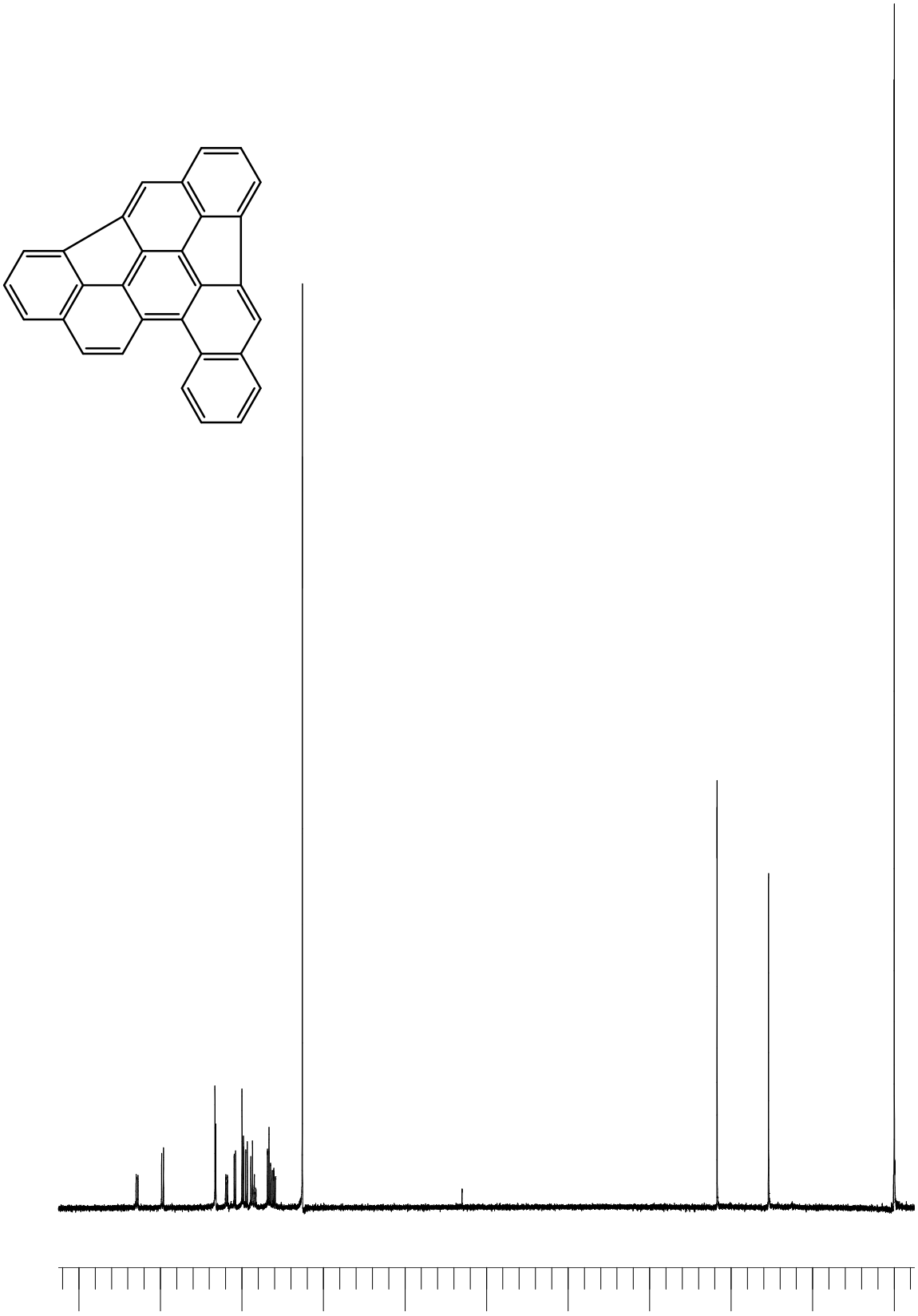
The solution was frozen-degassed three times at -78 ^{o}C. Zinc (159 mg, 2.42 mmol) and compound **6** (30 mg, 0.081 mmol) were added. The reaction was heated to 150 ^{o}C for 24 hrs. The solution was cooled and flushed through a silica plug with dichloromethane. The solvent was removed under vacuum. The crude product was purified by column chromatography on alumina with a 10%-50% methylene chloride in cyclohexane solution as the eluent. Removal of the solvent gave 18.8 mg (63%) compound **9** as a yellow powder, mp = 286 ^{o}C, 4.6 mg (15%) compound **10** as an orange power, and 4.4 mg (15%) **benzo[c]naphtho[2,1-p]chrysene (4)** as a yellow powder.

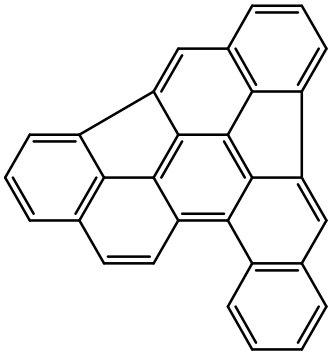
Compound **9**

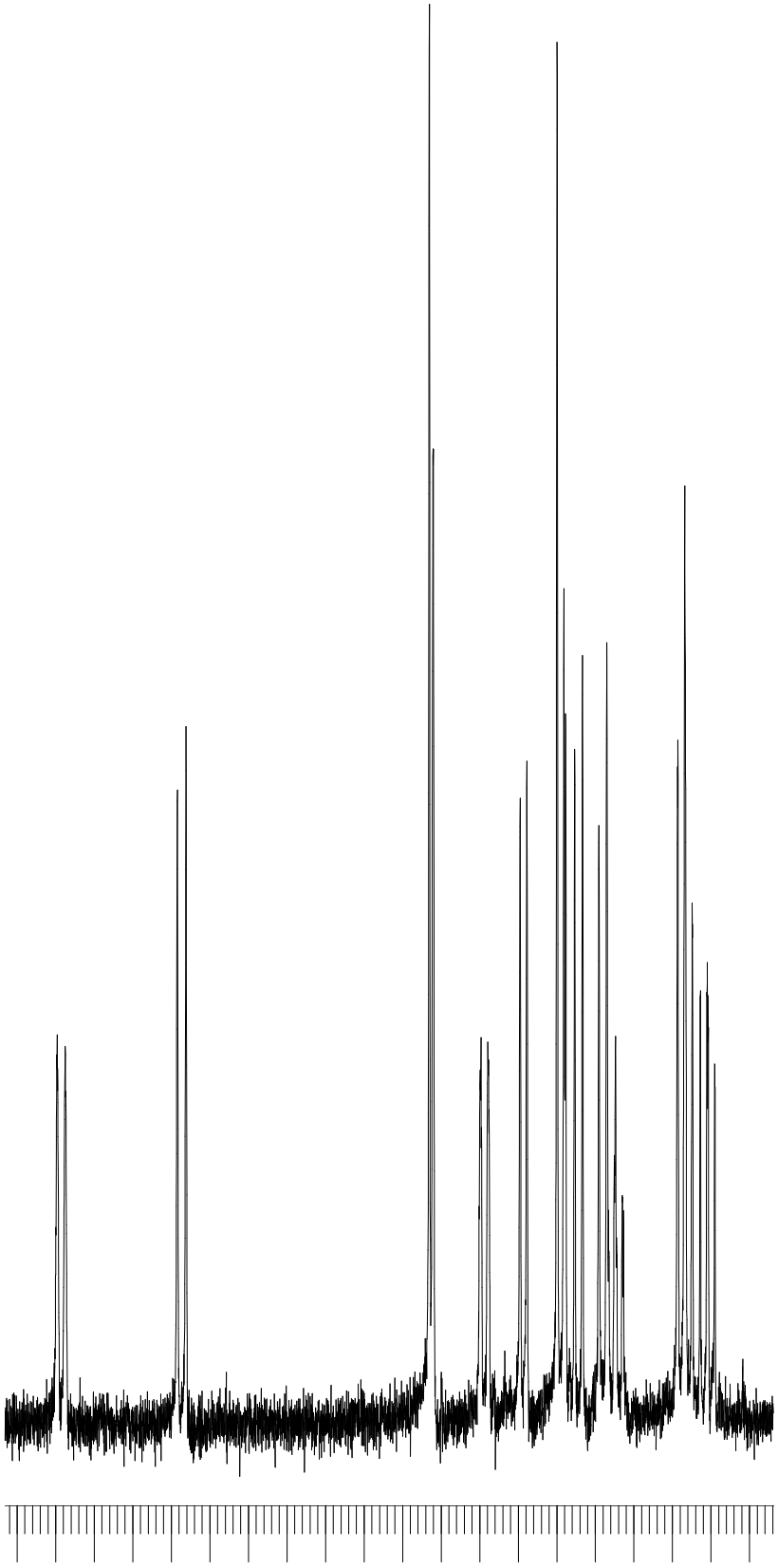
^{1}H NMR (400 MHz, $CDCl_3$)	δ 9.30 (d, 1H, J = 8.8 Hz), 8.97 (d, 1H, J = 9.2 Hz), 8.33 (s, 1H), 8.32 (s, 1H), 8.19 (d, 1H, J = 7.2 Hz), 8.09 (d, 1H, J = 7.2 Hz), 7.99 (d, 1H, J = 7.2 Hz), 7.98 (d, 1H, J = 8.8 Hz), 7.95 (d, 1H, 8.0 Hz), 7.88 (d, 1H, 8.0 Hz), 7.85 (dd, 1H, 7.2, 1.2 Hz), 7.67 (t, 2H, J = 7.2 Hz), 7.61 (dd, 1H, 7.2, 0.8 Hz)

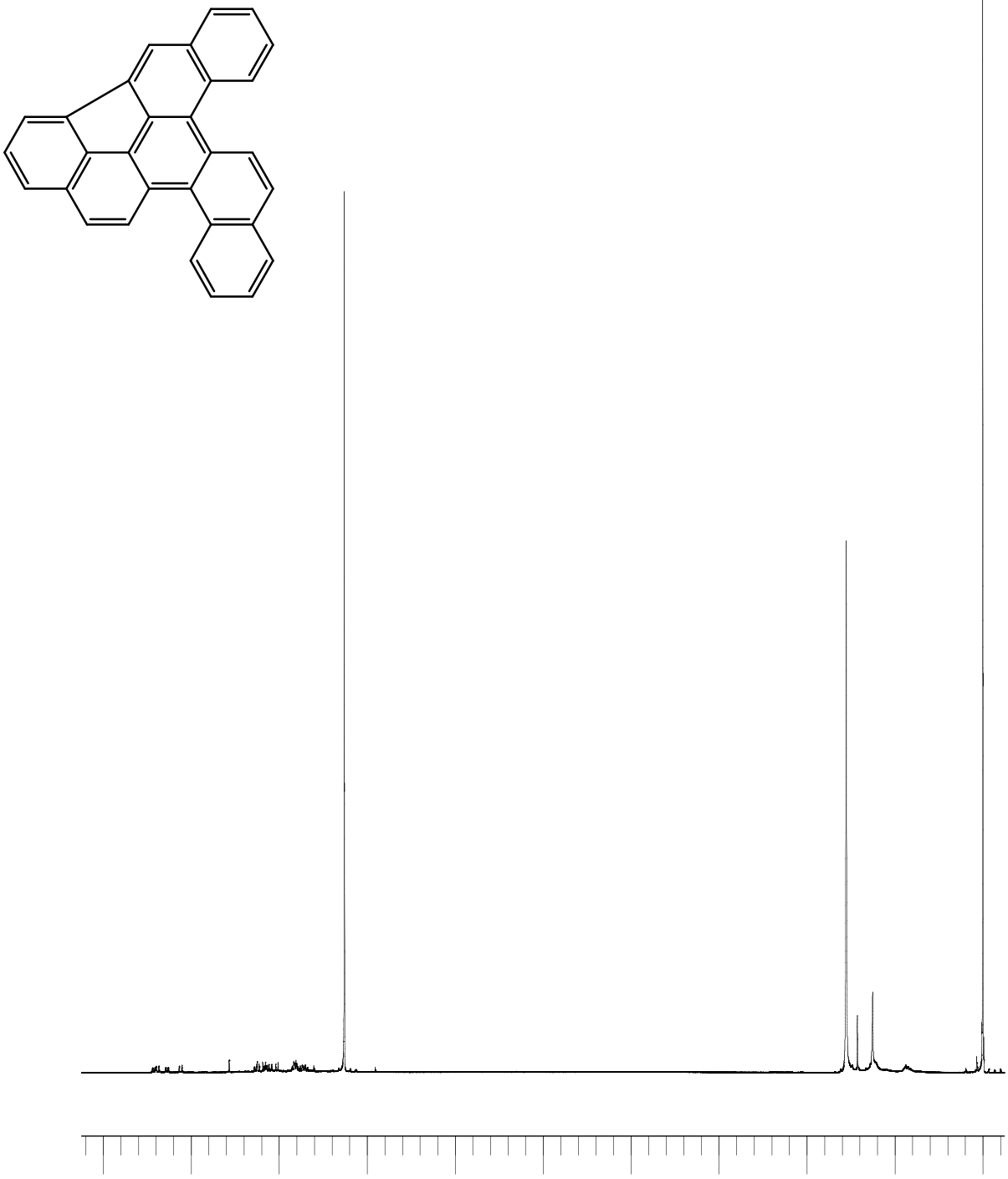
Compound **10**

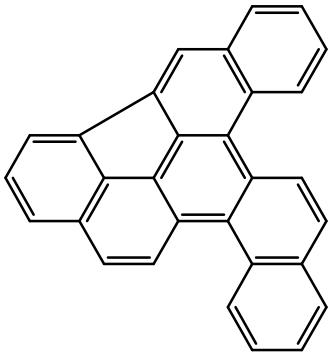
^{1}H NMR (300 MHz, $CDCl_3$)	δ 9.43 (d, 1H, J = 8.4 Hz), 9.39 (d, 1H, J = 9.0 Hz), 9.28 (d, 1H, J = 8.4) 9.13 (d, 1H, J = 9.0), 8.57 (s, 1H), 8.27 (d, 1H, J = 9.0), 8.24 (d, 1H, J = 7.2), 8.17 (d, 1H, J = 9.3), 8.16 (d, 1H, J = 7.5), 8.10 (d, 1H, J = 9.0), 8.03 (d, 1H, J = 8.1), 7.83-7.79 (m, 3H), 7.76-7.68 (m, 2H)

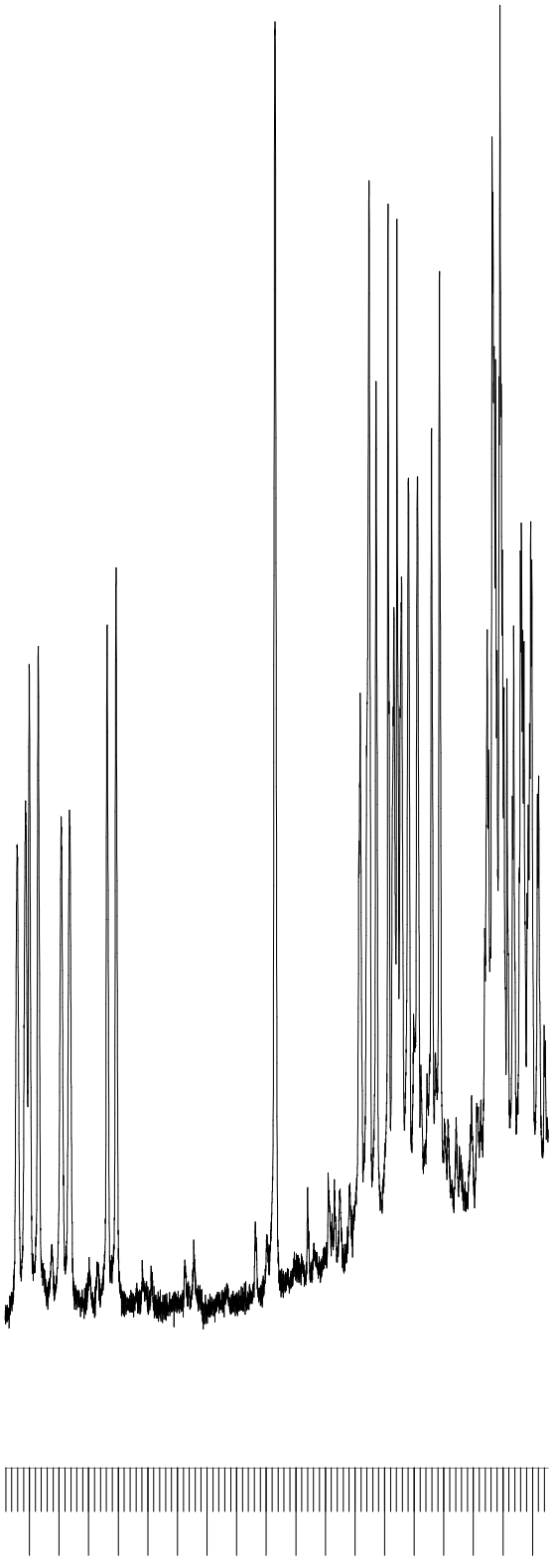




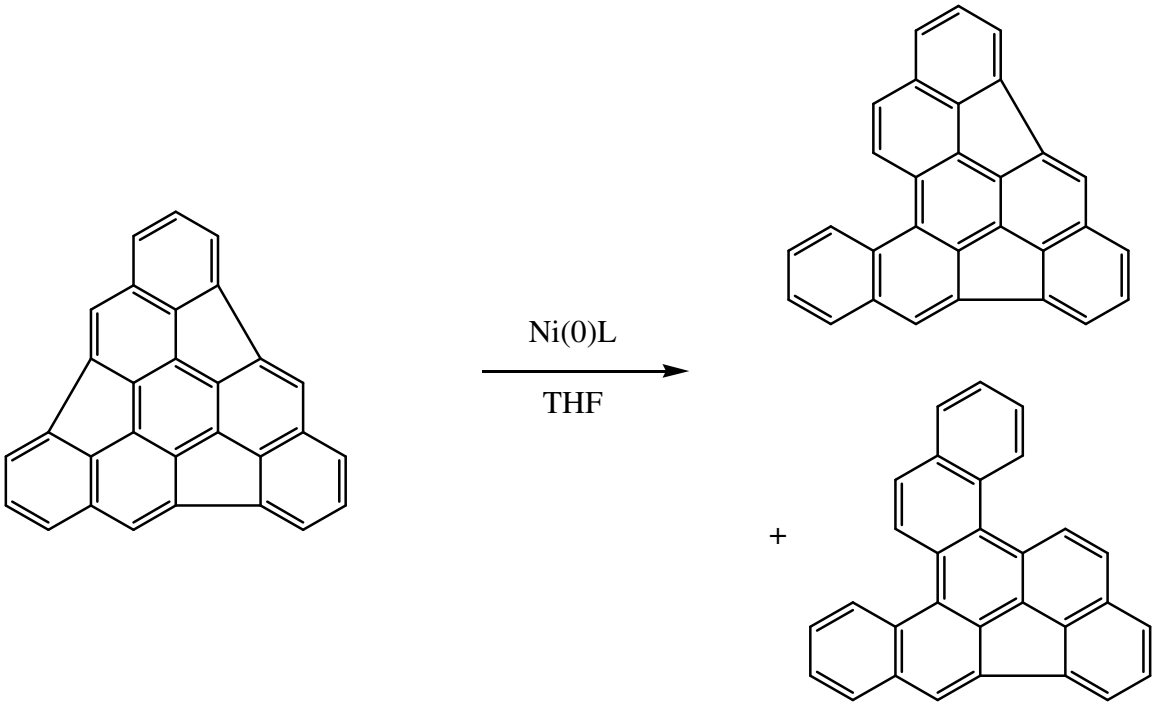








4.6.5. Nickel (0) General Procedure



In a dry 15 mL pressure vessel under nitrogen were added Nickel(II) acetylacetonate (21 mg, 0.081 mmol), or bis(diphenylphosphino) propane] nickel (II) chloride (44 mg, 0.081 mmol), tetrabutylammonium iodide (20 mg, 0.054 mmol), and the appropriate ligand (3 eq/**6** of dppm, 6 eq/**6** of $P(Cy)_3$). THF (3 mL) was added by syringe. The solution was frozen-degassed three times at -78 ^{o}C. Zinc (53 mg, 0.81 mmol) and compound **6** (10 mg, 0.027 mmol) were added. The reaction was heated to 150 ^{o}C for 24 hrs. The solution was cooled and flushed through a silica plug with dichloromethane. The solvent was removed under vacuum. The crude product was purified by TLC chromatography using 5% dichloromethane / cyclohexane as the eluent. The product ratios were determined by NMR integration.

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